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**"Bath exhaustion in metal-free leather processes"**

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# INTRODUCTION

In the last decades the industry at international level has made a change of mentality and the world has realized that the industrial system that was being carried out would be the cause in the future of the destruction of our planet.

The tanning industry has been one of the industries that have had to adapt to new ways of working because of the contamination of its waste. Apart from solid waste, the most polluting of the tanning industry is wastewater and the large volume used. Large amounts of wastewater with environmentally toxic contents and toxic to humans were devoted to the rivers. Treatments for these wastewater began to be implemented and much has been done in the processes to minimize the toxicity of the waters, but even so it is not enough.

It should be borne in mind that the tanning process most used worldwide (many sources indicate that 80-90% of world production) is from chromium salts, specifically chromium III sulfate. Apart from the large amount of chromium salts that are flushed in wastewater, there is a danger of the formation of chromium VI that can cause severe allergies in humans and can even be carcinogenic.

Alternatives to this tanning have been designed with heavy metals such as chromium and that would reduce this risk and of course would eliminate large amounts of chromium from the waters.

For years, leather known as wet-white is manufactured, which is chromium free and can even be metal free. Its manufacture is based on synthetic products from the chemical industry and vegetable extracts.

Comparing wet-white leather with chrome tanning, chromium-free tanning exhibits a much lower abiotic depletion potential and a smaller impact on the global warming potential and human toxicity potential, reduced due to the nature of the tanning vegetables and syntans, reducing carbon footprint and environmental impact (Shi, J; Puig, R; Sang, J; Lin W. et al 2016)(**1**).

It talks about ecological processes, eco-friendly, metal free leather, biodegradable, etc. Many new concepts those in many occasions are not well understood and confused.

Next it will define these concepts:

**Ecological** (R.A.E): Product made without damage to the environment, human health, health and welfare of animals and plants.

**Eco-friendly:** products and processes that meet the definition of "ecological". This word has been used commercially.

**Biodegradable** (R.A.E): That in condition of spillage, it can decompose in an aerobic or anaerobic way, such as food and garden waste, paper and cardboard.

Definitions by "*Real Academia Española".* **(2)**

**Chrome free leather:** Leather article that chrome has not been used in its manufacturing process.

**Metal free leather:** Leather article that no metals have been used in its manufacturing process.

Once clarified the concepts, they can be related to each other. Wet-white leathers are always chrome free, but depending on the process they can contain metals such as aluminum and zirconium. Despite this, there are wet-white processes that are free of metals, which means that no metal salt has been used in its manufacture.

It can be considered that all wet-white tanning processes are ecological and eco-friendly because the wastes are more environmentally friendly and less polluting than if the tanning were with chrome. It is wrong to say that wet-white leathers are biodegradable. It is not true. What is certain is that work is currently being done to obtain biodegradable leathers and this type of process will be similar to current wet-white tanning processes. For a leather to be biodegradable, what it will surely have to be is free of metals (metal free).

This study will work with wet-white, metal-free leather processes. It is true that this type of process is more ecological at the level of wastewater than chrome tanning processes, but this doesn't mean that the waters are not contaminated. The contamination with metals in the wastewater has been eliminated, but on the other hand the water is more contaminated with oxidizable organic matter that greatly increases the COD of the wastewater during the tanning / re-tanning and fatliquoring processes (wet-end processes).

Wastewater treatment plants receive wastewater from this type of tannage process and it have collapsed and have had to close floodgates because the biological and chemical treatments of the wastewater treatment plants are not enough to reduce these values of chemical oxygen demand.

For this reason, this study attempts to address this problem and achieve ecological processes metal-free but with lower COD contents in their wastewater.

# OBJECTIVE

The study *"Bath exhaustion in metal-free leather processes"* aims to conduct a study on the effect of different chemical products used in the tanning industry and different wet-end processes on a wet-white raw material, with a view to the contamination of the wastewater. The problem of contamination of wastewater in the tanning industry is well known and this study will seek to find solutions and relationships between processes and chemical products to reduce the amount of Chemical Oxygen Demand (COD) during the tanning processes and re-tanning on metal-free free leathers. The objective is to study the fixation and baths exhaustion in these processes, recurrent products (vegetable extracts, syntans, resins and biopolymers) and fatliquors. At the same time, it will also seek to design an ecological and reproducible in industrial level and a good metal-free article as a final result.

# THEORICAL ASPECTS

## 1. General information on the structure of the industry of leather processing.

Tanning is the process that converts the skin of the animal into leather. Tanning is essentially the reaction of collagen fibers with tannin, chromium and / or other tanning agents that are involved in the formation of leather.

The process for obtaining finished leather from fresh skin can be divided into multiple stages, which in turn can be divided into four phases: beamhouse, tanning, re-tanning and finishing.

The beamhouse stages for a conventional process are the following: soaking, unhairing and liming, lime fleshing, lime splitting and trimming, deliming and bating. The objective of this phase of the process is to clean the leather, remove adipose tissue and hair, and regulate the thickness of the skin to the desired value.

The tanning stages for a conventional process are the following: pickling, tanning, samming and splitting. The objective of this phase of the process is to partially degrade the skin structure to facilitate the penetration and subsequent fixation of chemical products, adjust the pH to the appropriate value for tanning, and stabilize the structure of the collagen by adding tanning products (the most frequent are chromium salts or vegetable extracts). In addition, for ovine skins, a degreasing is also done after pickling. After the tanning stage the leathers are already stable and in this they are called «wet-blue».

The re-tanning stages for a conventional process are: neutralized, re-tanning, dyeing, fatliquoring, draining and drying. In this state the leather is called 'crust'. The objective of this phase of the process is to adjust the finally desired thickness for the leather, achieve fullness and color characteristics, and bring the leather to adequate moisture content.

The finishing stages for a conventional process consist of various mechanical operations and / or the application of various products on the surface to give it the desired final texture and appearance.

Depending on the type of leather or raw material and the final product that you want to obtain these commented stages can be performed in various ways.

** bibliographic sources of official documents "Guia de Mejores Técnicas disponibles es España del sector de curtidos"* ***(3)*** *and "Guía de buenas prácticas ambientales. Industria del curtido de pieles"* ***(4)***

In the following figure there is in general terms a diagram of the different steps commented in the tanning process.

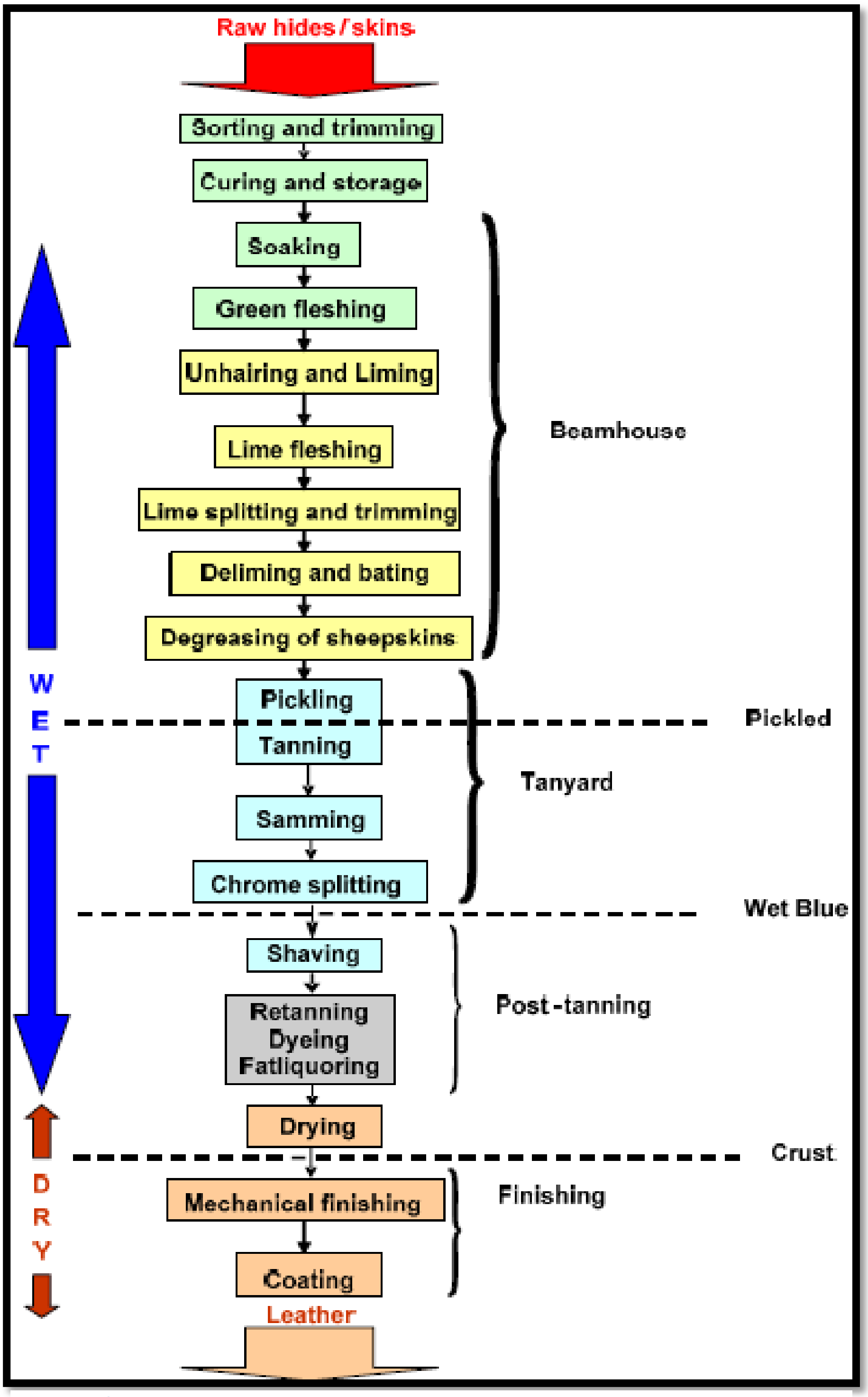



**Fig 1: Leather processes.**

Figure 1 of the official bibliographic source "*Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins*" **(5)**

- **Sorting and trimming:** Once the animal has been, the skin is separated from the rest of its body and until the skin reaches the hands of the tanner a series of treatments are applied that allow its temporary conservation.
  First of all, skins are classified according to their quality. The quality depends on the defects and damages that the skin has and that the animal could suffer when it was alive. There are several methods of classification.
  The trimming consists of cutting the parts of the animal that will not be useful. These are the head, the tail, the legs, etc.

- **Curing and storage:** The most common conservation treatments are drying and salting. Both one method and the other, seek the non-proliferation of bacteria in a fertilized field such as the skin.
  One method tries to dry the skin and the other to preserve it by means of common salt. Both procedures pursue dehydration of the skin to stop the bacterial growth.
  Once the skin is preserved it can be marketed.

- **Soaking:** It is the first part of the Beamhouse processes. The raw skins (salty, dried or fresh) are already in the tannery and it is decided to start with the tanning processes. The raw skins are dehydrated and the soaking consists in wet again and cleaning the skin of blood, husks, microorganisms, globulins, albumins, salt, among other products.
  The duration of soaking can vary greatly depending on the state of the raw skin.
  In this process are used moisturizers and surfactants, basifying products, neutral salts and enzymes, antiseptics, etc.

- **Green fleshing:** This operation consists of cleaning the flesh side of the skin from traces of meat and fat that may have remained in it. This is done with the help of a machine that carries a cylinder with blades.

- **Unhiring and liming:** They are two different operations but they are done at the same time.
  Unhiring consist to remove the epidermis and hair from the skin and the liming consists of a hydrolysis of proteins that produces a loosening of the fibrous structure of the collagen or, in other words, the liming "empties" the skin.
  The products most used for unhiring are sulfhydrate and sodium sulphide.
  These operations can be carried out at the same time in the drum with a single bath.
  After these operations, the skin becomes thick and in many cases it is used to perform mechanical operations such as fleshing and splitting.

- **Deliming and bating:** The skin contains alkalis in the liquids present between the fibers spaces and calcium hydroxide between the skin's fibers. It is interesting to eliminate them because if not, the skin can have absorption problems preventing a good subsequent tanning and causing defects in the final product. The deliming is carried out using that they form soluble compounds with alkalis such as ammonium sulfate, sodium bisulfite, lactic acid, etc.
  In the same bath it can perform the bating that aims to loosen the structure of collagen by adding proteolytic enzymes. The remains of epidermis and hair that were still on the skin are also removed. You have to be careful the quantity of enzyme and time depending on what the final article is.

- **Degreasing:** This operation is always performed on sheep and pig skins, which contain 10-30% natural fat (dry weight). Bovine skins have 2-3% fat that is removed in the other beamhouse operations and then the degreasing isn't necessary.
  If the fat is not removed well from the skin it can cause less penetration of products, dark spots on the leather and other undesirable effects that harm the final result of tanning.
  This operation is carried out in the drum after liming or after the pickling.
  The bath temperature is between 30-35 ° C and the surfactants directly emulsify the grease and then a warm water wash is performed to remove the emulsion.
  There are also other degreasing methods such as using solvents.

- **Pickling:** It consists of the treatment of skins in the drum with saline and acid solutions in the same bath. This operation definitely prevents the action of the enzymes of the liming and prepares the skin for tanning. The pickling will be more or less strong depending on the type of tanning to be performed and the pH that is needed.
  At the end of the pickling the skin is usually left at pH between 2 and 3.5. This degree of acidity would swell the skin due to osmosis, impeding the entry of products, but this is avoided with the previous addition of common salt until a bath of approximately 6-7 ºBaumé (density) is obtained.
  The products most used industrially are formic acid, sulfuric acid and sodium chloride.
  Once the pickling is finished, the skins are ready to be tanned.

- **Tanning:** Process of penetration into the skin of a tanning product by chemically increasing the crossings between the fibers so that the insolubility or indispensability of the skin in water increases. Thus the skin becomes a stable material with the organoleptic and physical characteristics for its application.

The collagen fibers are stabilized by the tanning agents, such that the hide is no longer susceptible to putrefaction or rotting.
The majority of tanning agents fall into one of the following groups:

- mineral tannages
- vegetable tannins
- syntans
- aldehydes
- oil tannage.

The most commonly used tanning agent is basic chromium sulphate ($Cr(OH)SO_4$). This leather is commonly called “wet-blue”, for its color.

The type of tanning process it will talk about in this study is a tanning without chromium or metals, also known as wet-white tanning. In the next chapters we will talk about this type of tanning.

- **Samming:** Once the leather is tanned and has rested, then goes on to some mechanical operations.
  The first is to samming the leather and consists of passing the leather between two cylinders surrounded by felt that press the skin causing the exit of the residual tanning bath located between the fibers. The humidity of the sammed leather is approximately 60%.

- **Chrome splitting:** When the skin is already drained, we continue with the operation of dividing the leather. The thickness of the leather is very high and for this reason it is divided into two parts: the upper part (the full grain) and the part of flesh (the split). A blade divides the leather into two and on the one hand the suede that is used for one type of items is marketed and is cheaper because the skin defects are less visible, and on the other hand the full grain, the part of more quality, is marketed.

- **Shaving:** After dividing there is still another mechanical operation to finish adjusting the thickness of the leather. The shaving is an operation that involves passing the skin between two mechanical cylinders, of which one is smooth, while the other has V-shaped blades that cut. With this operation you can regulate and equalize the difference in thickness from one part to the other of the same leather and also from one leather to another.

  At this point in the process, with the wet-blue already shaved, leather is sold many times internationally.

The subsequent operations serve to give value and define the article but starting from the same base that is wet-blue, chrome tanned leather.

- **Re-tanning / Dyeing / Fatliquoring:** The operations that will be explained below are the operations that give most of the properties to the final article. We can have full or empty leather, with or without break, for batting, hard or soft, touch tube or rag, determine the color, etc.

  As we start from the drained wet-blue, first of all, it must be wet-back again, using normally wetting surfactants together with a little acid and EDTA salt. If we don't want to re-tan with metal salts such as more chromium, aluminum salts, zirconium ... that a lower pH is needed, we proceed to neutralization. The neutralization operation consists of raising the pH of the leather around 5 with products such as sodium formate, sodium bicarbonate, synthetic neutralizers, etc. The pH is raised to 5 because most re-tanning products are anionic and would not penetrate the leather.
  Re-tanning substances tend to have a tanning character, but what is attempted is to modify certain properties of the leather depending on the item you want to get.
  The main groups of anionic re-tanning products are:
  - Vegetable extracts.
  -Syntans
  -Aldehydes
  - Resins
  -Biopolymers (new products)

  The dye consists in changing the color that the leather has due to the tanning products. Depending on the final article of the leather, the dye can be penetrated or not. This depends on the dye, auxiliary products, concentrations, temperature, pH, etc.
  Dye fixation is also very important.
  The most used dyes are:
  - Acid dyes (anionic)
  - Direct dyes (anionic)
  - Basic dyes (cationic)
  - Metal complex dyes (anionic)

  Finally, fatliquoring is the operation that lubricates the leather fibers with the aim of obtaining leather that doesn't break when is dry and has adequate flexibility and touch. The products used are fats.
  This operation is performed in the drum such as re-tanning and dyeing, adding the previously emulsified fats in hot water. The bath also has to be with hot water.

It is very important to choose the types of fats and the percentages used, since by modifying these parameters you can obtain different final articles.
The origin of fats can be vegetable, animal or synthetic.

There are an infinite number of products for re-tanning, dyeing and fatliquoring. The chemical industry that is dedicated to this sector is very powerful and the competition and the quantity of products very high.
In the following chapters we will talk more about these products that are the ones that will influence our study.

After these three operations, the leathers are left at rest for at least one night, well stretched on an easel, to drain and increase the fixation of the products. Then we will go to the drying and mechanization operations.

- **Drying / mechanical operations:** Drying and subsequent mechanical operations are decisive for defining the final article.
  Normally, after the leather has rested, it is samming. The leathers pass through a machine that has two cylinders coated with felt. When the leather passes between them, it expels part of the water it contains due to the pressure. This operation also opens the leather and leaves it completely flat and wrinkle-free, maximizing the surface.

  Then the process continues with drying operations that the objective is to evaporate the water that the leathers contain. There is a lot of variety of drying methods. Some of them are:
  - Hang dry.
  - In camera / tunnel.
  - By heat pump.
  - Pasting
  - Secoterm.
  - Vacuum.
  - Etc.

  Once dry, mechanical operations can be performed to give a series of features before the leather is finished.
  - Conditioning (give moisture).
  - Softened.
  - Final drying.
  - Buffing.
  - Milling.
  - Etc.

Once all the operations we have spoken are over. All wet processes would be terminated. The leather we have at the moment is called **"crust".**
The leather is now ready to be finished if required by the article.

- **Finishing / coating:** It is understood by finishing a set of operations based on the surface treatment of leather to give it the final appearance with which it is marketed. Therefore, the finish affects the visual appearance, touch and physical properties of leather.
  The finishing operations are endless, just like the variety of items that can be made with a host of products of a very different nature.

  In this study we will not perform finishing operations. The leather will remain in crust.

*Tanning processes of the bibliographic source by MORERA.J.M "Química Técnica de Curtición"* **(6)**

# 2. Wet-white tannage

As it has seen in previous sections, in this industry exists different methods of tanning. Animal skins are converted to leather through numerous mechanical and chemical operations which are divided into three sub groups: beam house, tanning and post tanning.

Tanning is the process of the transformation of putrescible pelt into stable material leather, capable of resisting microbial attack. Then in re-tanning processes is where the most specific characteristics are given to leather.

The wastewater from chrome tanning operations contains 35-40% chromium of total offer. Furthermore, the using technology of chrome containing tannery solid wastes to useful byproducts also discharges this heavy metal to the environment.

This high amount of chromium ($Cr^{3+}$) is toxic for the flora and fauna and for the soil microbiology. In addition, various researchers have identified the possibilities of conversion of chromium (III) to its hexavalent ($Cr^{6+}$) state during tanning. This molecular state is carcinogenic for human and it has toxic and mutagenic behavior to the microorganisms and aquatic systems.

Today it exist possible alternatives of conventional chrome tanning method. One of them, is wet-white tannage.

Bibliographic source by KUMAR, R; Md TARIKUL; SARKAR, P; Md SHAHIDUL, *Production and quality enhancement of wet white leather by syntan assisted polyphosphate tannage: A cleaner technological approach to the leather processing* **(7)**

The description of wet-white leather for the official document of *"Pollution Prevention Opportunities in the Tanning Industry within the Mediterranean Region"* **(8)** is:

> *" **Description :** One way of tanning the hides is by relying on chrome free methods. Leathers tanned through these methods usually have a whitish color and represent a series of ecological advantages.*
>
> *Ecological advantages of wet white:*
>
> *· No restrictions on dumping or potential incineration of solid waste (shavings and trimmings).*
>
> *· Solid waste can be composted.*
>
> *· No need to recycle chrome.*
>
> *· Wastewater does not have to be pre-treated to precipitate chrome.*

*In addition to the advantages found in the final elimination of chrome needed in the conventional tanning process, the full polymer technique presents the following advantages:*

*1- Excellent exhaustion and fixation*

*2- Leathers can be dyed to high level, brilliant shades*

*3- Excellent light fastness.*

*4- Best results are obtained for perspiration resistance and wash fastness in comparison with other chrome-free systems.*

***Issues to consider when selected:***

- *The final quality of the leather product has to be taken into consideration, as the wet-white will lead to a different texture suitable for specific types of leather production.*
- *Due to reduced heat resistance, the drying of the chrome-free tanned leather has to be done carefully. The end product is not suitable for the manufacture of vulcanized footwear.*

***Wet-white tannage:***

*Environmental Benefits*

- *Reduction in the level of chemicals found in effluents.*
- *Reduction in hazardous solid wastes."*

One method of wet-white tanning  is a metal-free process. These leathers are called metal-free. In this process doesn't use nothing of chromium, it doesn't use also aluminum, iron, zirconium, etc ... Its production is made from synthetic substitutes and auxiliaries, polymeric resins, vegetables extracts, and those known as biopolymers. This process produces a finished article that is not only equal to metal-bases tanning procedures, but actually far surpasses them in many fields.

The main difference for this reason in terms of leather, is that the shrinkage temperatures of wet-white processes including metal-free, are lower. They will hardly reach 90ºC, when with chrome we exceed 100ºC. This could be a problem for some type of article. Then the structure, fullness, compactness of the leather is not the same with one process or with the other, but this already depends on the article that is sought if the chromium-free process is valid or not and also know how to give those characteristics in the processes post tanning. The technicians and the chemical industry technicians have an important role here.

The subject of this study is largely environmental. In the wastewater there will be no metals because the processes will be free of metals, but on the other hand other types of products are used that also pollute the water at an organic level and this can also become a serious problem.

# 3. Chemicals used in wet-white tanning processes.

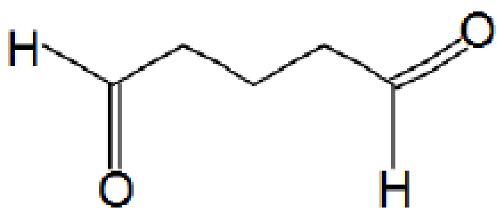
In the previous chapters it has seen all the steps of a standard tanning process and then it has talked about wet-white in general terms. In this chapter it will go deeper into how this type of tanning is and will talk about the chemicals used and their characteristics.

## 3.1 Aldehydes.

Of the aldehydes with a strong tanning capacity, the best ones are: formaldehyde, acetaldehyde, glyoxal, methylglyoxal, starch aldehyde, oxazolidine and alpha-hydroxyatypic aldehyde; each of them with very different chemical structures, as well as different number of aldehyde groups, which gives each one different tanning and organoleptic.

The aldehydes react with the basic groups of the collagen, which are not charged from the point of electric sight and their combinations are strongly influenced by the pH of the solution, concentration and time in which it is in contact with the skin.

It will work with glutaraldehyde, glutamic aldehyde or 1,5-pentanedial. Its structure corresponds to:



$C_2H_8O_2$

Fig 2: glutaraldehyde

In aqueous solutions, glutaraldehyde doesn't have this open structure but undergoes modifications. As a monomer, it adopts a cyclic structure that is stabilized with a hydrogen bridge.

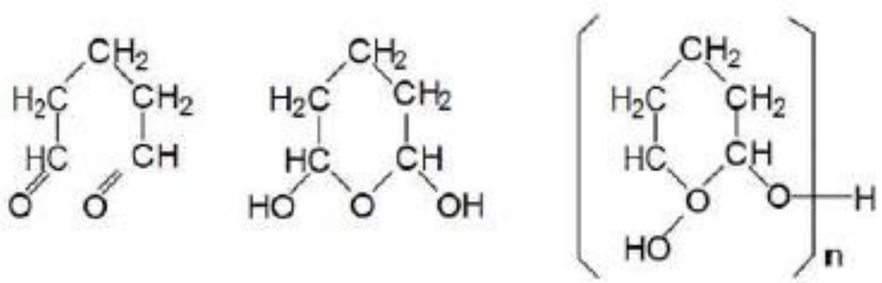




Fig 3: glutaraldehyde cyclic structure

Three important conclusions can be drawn, that in aqueous solutions, glutaraldehyde is disposed in its linear structure or as a dialdehyde monomer in a limited way, that glutaraldehyde forms a, b-unsaturated aldehydes and finally, which polymerizes rapidly (and in a form irreversible at pH> 8-9).

Normally the pre-tanning for manufacturing FOC articles or organically tanned leathers begins with the use of glutaraldehyde.

In the figure below, the reaction of aldehydes with the amino groups of collagen is observed.

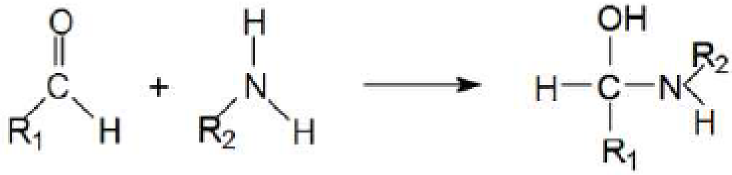


Fig 4: glutaraldehyde reaction with amino groups

Many attempts have been made to develop wet-white leathers using other tanning agents than C but it has been found that alone the aldehydes are in a position to compete with the mineral tanning agents.

Small amounts of pure glutaraldehyde (100%) between 0.5-1.0% on shaved weight are sufficient to pre-tan; facilitating the exhaustion of tanning baths and the recesses obtained are biodegradable.

With regard to the issue of shrinkage temperature and other properties that define the quality of a wet-white leather, it has been demonstrated that a polymeric tanner that resists these pH conditions is used together with the glutaraldehyde.

The concentration of aldehyde added is also a very important factor considering the physical properties of resistance to grain bursting and tearing. Also the more aldehyde applied, the leather is more yellow.

It isn’t common apply product with a concentration of more than 50% of active matter.

*Bibliographic source of the article “Curtición Wet-white”* ***(9)***

## 3.2 Vegetable / syntan tanning

Vegetable tanning extracts (liquids, solids, dust) are extracted with water and subsequently concentrated. Its characteristics can be determined by the tannic analysis that will allow us to obtain the percentages of moisture, insoluble matter, non-tannins, tannins and the values of pH, acidity and salts.

Tanning extracts solutions generally have a more or less high percentage of water-insoluble substances that can be found in the form of a suspension or precipitate, which can come from the plant material itself, be formed in its extraction process or during the manufacture of the leather. When they come from the extracted plant matter, they are tannins of a high degree of polymerization and cannot be kept in suspension due to the peptizing effect of the other components of the extract.

The fundamental component of tanning extracts is tannin that is the substance of transforming skins into leather. Tannins are highly complex polyphenolic compounds that can have very different compositions and structures depending on their origin.

In tannic extracts, together with tannins, non-tanning substances are found that have been separated from vegetables during the extraction process. These materials, called non-tannins, are constituted by carbohydrates of various types, organic acids, simple phenols that did not reach the molecular magnitude of the tannins, Lignin proteins and compounds. Among these non-tannins there are substances that are not absorbed through the skin, but which during the tanning process can evolve and transform by polymerization into true tannins.

Insoluble substances are substances that don't solubilize in water, but which because of their small size do not damage but favor tanning or give weight.

The insoluble substances that the tannins have help the tanning, because if what we use as tanning substance were 100% tannic substance, tanning substance, it would be produced (although these were conditioned to the ideal pH of the tannins, about 4.5- 5) a superficial over-tanning that would prevent the passage of the tannins inside. All these non-tannin substances are those that favor the penetration of tannin and prevent over-tanning.

Among the commercial tanning extracts we find:

- **Pine extract:** great astringency, gives the leather a reddish color

- **Oak:** gives firm yellowish brown hides.

- **Sumac:** is a soft extract that penetrates quickly into the skin, gives leather soft and flexible touch and very light color.

- **Walloon:** of great astringency gives quite waterproof yellowish leather

- **Chestnut:** high astringency, gives firm leathers of hazelnut color. This extract is the most solid in light

- **Mimosa:** easily soluble in water, gives flexible beige leather

- **Quebracho:** gives firm leathers, cold soluble by bisulfitation gives more flexible and soft leathers.

- **Tara extract**

**SYNTANS**

Synthetic tannins or syntans are also used as pre-tanners which, having the small molecule, penetrate before and very quickly, before natural tannins that are formed by colloids of much larger structure. These pre-tannin tannins open the way and favor penetration. That is why it is common to use them previously as pre-tanners and can also be put together.

Organic synthetic tannins are non-natural organic chemicals that transform the skin of the animal into stable leather by chemically modifying the collagen. They are also called **syntans**.

These products can act as tanning, re-tanning, bleaching, dispersing, etc.

The aromatic chemical bases that constitute the synthetic tannins are of the type benzene, naphthalene, naphthalol, toluol, cresol, etc., and as condensing agents are used formalin, acetaldehyde, benzaldehyde, urea-formol mixture, etc.

They can be classified into two groups. On the one hand there are the **auxiliary synthetic tanning** agents that are condensation products of sulfonic acids (phenol sulfonic or naphthalene sulfonic) with formalin and these don’t tan. When mixed with other polyaromatic tanning agents, they accelerate penetration, disperse poorly soluble tanning agents and clarify the color of the leather.

The ones we will study are those that correspond to the other group: the **replacement syntans**.

These syntans are synthetic organic products that can theoretically replace vegetable tanning agents in any of their applications.

In general they are more solid in the light, they clarify the color of the leather, they have smaller molecules which makes them less filling, and with a tendency to give less hard leather. Being more anionic, they clarify the dyes but change the tone less. They are useful for a bleaching of chromed leather when you have to make dyes in very light tones. There is a great variety on the market that goes from some very astringent and dehydrating to make nicks, going through normal and white synthetics with a good bleaching power, to very little astringent and light-synthetic synthetics, which allow re-tanning in skins type clothing or upholstery, whose light fastness should be good and its touch very soft.

Many times mixed vegetable-synthetic in re-tanning are made to be able to take a bit of the advantages of both, being in general what is sought is the greatest filling of the vegetable and the soft touch and the light fastness and lightening of the color of the synthetic.

The quantities used are analogous to those of vegetables 4-6% but it must be in many cases they are liquids of 50-60% solids richness or less (30%), which then causes quantities of the order of 15% aprox. 12% if used alone, or replacing 1% of vegetable extract with 2% of synthetic liquid substitution.

The molecular size is decisive for the tanning property of the syntans. If it is too small, transverse links between collagen chains cannot be established and if it is too large there are steric hindrances and cannot penetrate.

*Bibliographical sources are website "Cueronet" **(10)** and MORERA, J.M "Química Técnica de curtición" **(6)**.*

## 3.3 Resins

The processes with resins generally produce more filling and may not decrease the intensity of dyeing so much. They have a tendency to selective filling in the emptiest places of the skin due to their high molecular size, which sometimes makes their solutions colloidal, and even almost suspensions.

In the market there is a wide variety of resin-based products and chemical companies are constantly developing new products for re-tanning.

Resins according to their charge can be classified as anionic, cationic and amphoteric.

We will study the anionic resins that are the most commonly used and the ones we will use in our study.

<u>Anionic resins</u>

They generally belong to acrylics or similar and their degree of anionic is very diverse since they can be slightly anionic if they are emulsions of uncharged resins in which the only anionic is the emulsifier or products with sulphonic and / or carboxyl groups, which they give them a considerable anionic character. They belong to the group of polymers or pre-polymers very advanced in their degree of polymerization. Its solubility in water is variable, from those that give true solutions to those that are only suspensions or emulsions. They are fixed in the fiber by its charge and also in some cases by covalent bond as true tanning products. At acidic pH (pH = 3.54) they increase their fixation both by the change in skin charge and by the molecular aggregation that occurs when their solubility decreases, especially in pre-polymers.

In relation to their behavior against the skin, they differ from the vegetal and synthetic tannin extracts, their lower negative charge, their greater filling and fiber adhesion power, their lower astringency, their tendency to give gummy touches, and their solidity to the light mainly. In the most insoluble state, its tendency to deposit almost physically in the empty parts of the skin.

They method of application is the same like vegetable extracts or synthetic tannins. They are frequently used together with them in mixed re-tanning.

At the time of the resin addition, the leather pH should be around 5; therefore, in many cases they are used in dyeing, the resin is added first, alone or together with the synthetic or vegetable and then formic acid. If the resin is not pH sensible, it is added mixed with vegetable or synthetic extracts.

*Bibliographical sources are website "Cueronet"* ***(10)***

## 3.4 Biopolymers

Biopolymers are a new generation of products in the tanning industry. These products come from the protein extracted from the one of the residue of this industry, chrome shavings. Chrome shavings being the major waste generated from chrome tanning solid waste. Proportion of chrome shavings produced are strongly dependent from the kind of article and the process used in the tannery (53 kilograms / per 1000 square feet).

The use of protein chemical derivatives are for cosmetics, textile and leather applications, is really old. Some very well-known and very traditional re-tanning agents are based on proteins from many different origins. First chemicals and patent applications talking about recovering protein from chrome shavings and trimmings are as old as from before 2nd world war, only some few years after introduction of chrome tanning process. But this different origin and treatment will also mean very different properties when applied into the leather, reactivity, fixation and stability should be really different.

Most of them will show an *amphoteric behaving coupled with a characteristic iso-electric point as also shows leather.* These properties will confer to these chemicals strong reactivity with leather, both chrome and vegetable tanned hides. The *molecular weight of the obtained polymer will also be critical, and* choosing it correctly allows imparting very different properties to the chemicals and to the leather.

All chemicals obtained by this procedure will show many benefits from the environmental and ecotoxicological point of view. They are free of formaldehyde, have and excellent biodegradability and an excellent biocompatibility with skin and mucosa.

Collagen hydrolyzed could be modified and reacted in many different ways and depending from these reactions is possible to produce re-tanning agents, wetting tensides or fatliquors for leather.

Chemical benefits:

- No mineral component.
- Zero discharge.
- Not food concurrent.
- Low carbon footprint.
- High biodegradability.
- No regulated components (formaldehyde, phenol, etc).

## 3.5 Pre-tanning

Pre-tanning in wet-white processes consists in stabilizing the collagen in some way in order to samming, divide and shaving. From there you can market the leather. It would be similar to the moment we have wet-blue in chrome tanning, but the difference is that a wet-white pre-tanned leather doesn't reach such high shrunken temperatures and it still has to perform the main tanning and then re-tanning.

There are several types of wet-white pre-tanning processes, but this study will talk about a pre-tanning with aldehydes, syntans and resins. As previously mentioned, it will not use any product with metals.

The process starts from pickling skins at a pH of 3.2-3.5 and in the same bath is added between 1-2.5% glutaraldehyde, plus between 2-6% a mixture or individually of an acrylic polymer and a synthetic phenol base. With the addition of the polymer, the distribution of the glutaraldehyde is improved in a more homogeneous way, obtaining a Tg between 70-75 ° C. It runs 3-5 hours until the total penetration uniformly, then it is passed to the fixing phase where the pH is increased to values of 3.9-4.5 by the slow and controlled addition of a sodium bicarbonate solution or it can also be sodium carbonate. It is important to control the final pH since pH higher than 4.5 would cause excessive polymerization. Therefore a much more intense and persistent yellow color that would disturb when obtaining certain light colors or pastel colors; in addition the grain would be more fragile.

The addition of the synthetic phenolic, helps during the draining to improve the dehydration of the leather and therefore to positively regulate the shaving process, in addition to obtaining firmer grain leathers and greater fullness.

Then the leather would be rest (horse up) and they would proceed to the mechanical operations of samming, dividing and shaving.

## 3.6 Tanning / re-tanning

The tanning and re-tanning of wet-white leathers is often done together. It might be in the same bath or in separate bath but it is part of the same process.

There is no standard process, depending on the final article can vary greatly. The products we have spoken before are combined to give some characteristics to the leather. The process can vary greatly if the final article is intended for automotive, footwear, garment, leather goods.

The process that it will work in this study could be directed to more than one type of article.

It is this part of the process, re-tanning and tanning, where it will study how the products and the process affect the contamination of wastewater.

In the next chapter it will see the contamination of the water and its possible treatments in the tanning industry.

# 4. Wastewater in tanning industry

In all processes in leather industry water is the main medium of transport for the chemical.

Many of the processes in the tanning industry use a large amount of water. This industry uses between 30 -40 L of water per kilogram of processed leather.

Globally this industry uses 300-500 billions of liters. For this reason, the high consumption and high pollution of wastewater combine this sector in one of the most polluting at the manufacturing level and it is necessary to apply a lot of water treatments.

Pre-tanning operations consume about 15-22 L of water per kg of leather, while tanning operations consume 1-2 liters per kg of leather and re-tanning operations 1-2 liters per kg of leather. To all these quantities of water must be added the intermediate washings of the processes and this amount is around 11.5-13 liters per kg of leather.

In the following table there is a summary of the amount of water consumed in each stage of the tanning process:

Table 1: consumption of water

| Operation | Quantity ($m^3$) |
|---|---|
| Soaking | 9.0–12.0 |
| Liming | 4.0–6.0 |
| Deliming | 1.5–2.0 |
| Pickling | 1.0–1.5 |
| Chrome tanning | 1.0–2.0 |
| Neutralisation | 1.0–1.5 |
| Wet finishing | 1.0–2.0 |
| Washings | 11.5–13.0 |

Each of these operations provides distinct contaminants to wastewater because the chemicals used in each process are different.

The water treatments performed are a temporary and mandatory solution but other technological options are investigated to reduce water use and try to change processes.

There is a lot of pressure from environmental agencies for the amount of toxic pollutants in the water and that require a decrease in biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total dissolved solids (TDS).

To maintain the quality of water, cleaner technologies are beginning to be applied in the tanneries to minimize the consumption of water and its contaminants.

The best strategy to combat this serious problem is to work with cleaner processes and apply good practices to reduce the costs of water treatment in treatment plants.

*Bibliographical source of official document by RAGHAVA, J; CHANDRABABU, N.K; MURALIDHARAN, C; UNNI NAIR, B; RAO, P.G; RAMASAMI, T. "Recouping the waste-water: a way forward for cleaner leather processing". **(11)***

Then it will talk how to reduce and how it affects water pollution in the tanning and re-tanning phases in wet-white leather.

**Synthetic organic tannages and vegetable tannages**

Synthetic are sulphonated condensation products of hydroxyl-substituted aromatic compounds (phenol, cresol, naphthalene, etc) with formaldehyde and often amides. Although some syntans are easy biodegraded, others are recalcitrant. Those with lower potential environmental and human health impact are available commercially, but better alternatives have yet developed.

On the other hand, in contrast to chrome tanning, there are vegetables tanning and these processes require large amounts of tanning agent. The effluent produced from vegetable tanning is dark and turbid, and contain a higher load of poorly biodegradable COD than chrome tanning effluent. However, vegetable and syntan tanned leather are easily biodegradable and compostable as tannins are common in decaying plant materials.

**Wet-finishing (re-tanning wet-white)**

The implementation of advanced re-tanning methods is aimed at reducing the pollution load of, sulphates, COD, suspended solids and nitrogenous compounds.

Optimization of industrial wet-finishing systems (re-tanning, dyeing and fatliquoring) is required to achieve the lowest possible COD and salt levels in the effluent. Optimization high-exhaustion re-tanning methods using appropriate masking agents and amounts (to avoid difficulties with the precipitation) should be implemented. The addition of amphoteric polymers improves the exhaustion of dyes and fatliquoring agents, and has been shown to reduce the COD discharged.

Use of biodegradable re-tanning agents that produce quality leather with desired properties should be prioritized as alternatives to chrome. Re-tanning compounds based on urea-formaldehyde or melamine-formaldehyde resins, or amino resins should be replaced with non-nitrogenous compounds such as acrylics polymers. This may reduce the ammonia load. The introduction of organic chemicals and preparations with limited biodegradability, high COD values, and dyes containing toxic metals such as lead, cadmium and Cr (VI) for wet finishing should be avoided. Fatliquoring agents based on chlorinated paraffin, benzidine and other azo dyes (which may be reduced to carcinogenic amines) and those with oxidizing properties should also be avoided.

*Bibliographical source of official document by SWARTS, C.D; JACKSON-MOSS, C; ROWSWELL,R.A, MPOFU, A.B. "Water and wastewater management in the tanning and leather finishing industry"* ***(12)***

## 4.1 Wastewater pollution parameters

A wastewater influences the environment where it is poured due basically to five parameters. Oxidizable matter, which consumes oxygen. Solids, which hinder the biological activity of aquatic beings and the recharge of aquifers. Inhibitory or toxic substances, which inhibit, modify or cancel biological activity and / or can accumulate in the food chain. Nutrients (N and P) involved in the eutrophication processes. Salinity which can affect the transfer of matter between the environment and cells. Others such as the temperature of spills and fat content may also be important.

Consequently, the characterization of a wastewater is carried out with respect to all these parameters.

### *4.1.1 Solids*

The measurement of the particles determines their specific surface, the relationship between them is quadratic, and the specific surface is related to the decantation time.

- TOTAL SUSPENSION SOLIDS

Solid fraction that does not pass through the 0.45 µ filter.

- Settable suspended solids.
- Non-settable suspended solids.

- DISSOLVED SOLIDS

It would be better to define them as filterable solids, they are those that are not retained by the filter and we can distinguish between them:

- Colloidal solids

- Dissolved solids

- TOTAL SOLIDS (ST)

Sum of both. For all cases and according to volatility at 600 ° C, an organic and inorganic fraction is distinguished, the latter remains in the form of ash.

### 4.1.2 Inhibition matter

They can present toxicity or inhibit the biological processes a large amount of chemical compounds, both organic (aromatic, phenols, aldehydes, organohalogenates, phytosanitary products, etc.) and inorganic (heavy metals, Hg, Cd, Cr, Zn, Cu, etc. Anions: CN-, S =, etc.). To detect this toxicity we have the tests with Daphnia and with bacteria (microtox), although it is always good to know the origin of the water to be able to determine these toxins safely, try to avoid them and prevent treatments.

Inhibitory materials may influence BOD measurements, presenting lower or no results, and giving erroneous analysis results.

### 4.1.3 Nutrient (N I P)

The nitrogen compounds: ammonium and organic nitrogen, which are presented in the analysis such as NTK (total Kjelhdal Nitrogen), come from both urban and industrial discharges, the origin of nitrites and nitrates is basically industrial, in sewage treatment plants and rivers they can generate nitrates by oxidation of ammonium or organic nitrogen. Phosphorus compounds generally come from urban waste, phosphates and polyphosphates found in the detergent formulation. These nitrogen and phosphorus compounds may appear in the waters as diffuse contamination of agricultural and livestock activities.

N and P act as nutrients in plant species, so with atmospheric $CO_2$ and these nutrients can grow algae in the water, generating organic matter (degradable matter that consumes oxygen) from inorganic components, is what is known as processes of eutrophication.

### 4.1.4 Salinity

Salinity can modify the growth of microorganisms, since it influences metabolic processes, changes in it alter matter transfer processes due to differences in osmotic pressure. It is a difficult parameter to correct in wastewater, so its best treatment is prevention.

Other parameters such as temperature, grease, surfactants, etc. They can influence the purification processes, so it is convenient to know their values and take them into account in the treatment plants.

### 4.1.5 Oxidizable matter

#### BIOLOGICAL OXYGEN DEMAND (BOD)

It measures the amount of oxygen consumed by bacteria by degrading organic matter. It is a milder oxidation than the COD and only measure biodegradable compounds. Normally they express two values of it, $BOD_5$ and $BOD_{21}$ and express the oxygen consumption at 5 and 21 days.

$BOD_{21}$ represents in the majority of cases the total or final BOD, even though it is usually worked with $BOD_5$ that represents about 70% of the total BOD, always depending on the water analyzed.

There may be problems in determining the BOD of industrial waters, due to the presence of inhibitors (salts and toxins) or the need for acclimatization of the bacteria. BOD values greater than 2000 ppm are inaccurate since it has to be diluted very much the sample to carry out the test.

Other measures related to oxidizable matter or organic matter can be carried out, such as: Total oxygen demand (DTO) and total organic carbon (TOC). Both are instrumental methods.

#### CHEMICAL OXYGEN DEMAND (COD)

It measures the amount of oxygen equivalent to potassium dichromate used in the oxidation of a sample of wastewater. It is an intense reaction in which most of the organic matter is oxidized, between 95 and 100% (it does not oxidize: pyridine, benzene, ammonium, ...), it also oxidizes some inorganic compounds such as sulfides, cyanides etc. The units in which it is expressed are ppm of oxygen.

*Bibliographical source of "Tema 2. Parámetros de contaminación". **(13)***

The chemical oxygen demand is the parameter that we will analyze in our study. As we have seen, during the tanning and re-tanning processes the COD is the main factor to try to reduce and the most influential. In wet-white as vegetable and synthetic products that are organic are used, products that have not just been fixed on the leather increase the chemical oxygen demand of the wastewater. This is the parameter that we will try to find a way to reduce in this study.

The official method of COD analysis is according to ISO 15705. Kit "Nanocolor COD 15000" is used and it has an own method but based on the ISO standard. **(*Look Annex 2)***

Chemical oxygen demand is the measure of the oxidizable organic matter content of a wastewater sample. The sample is reacted with an acidic solution of potassium dichromate in the presence of a catalyst (silver) and digested for 2 hours at a temperature of 150°C. Oxidizable organic compounds reduce the dichromate ion ($Cr_2O_7^{2-)}$ to the chromic ion ($Cr^{3+).}$
In the commercial kits to measure COD, the decrease in dichromate ion is measured calorimetrically. The amount of chromic ion produced is measured. The test results are expressed as the number of milligrams of oxygen consumed per L of sample (mg $O^2$/L ).

The samples must be collected in glass containers and if they are stored, they must be acidified with concentrated sulfuric acid to pH <2 to pause the decomposition and not increase the oxidizable organic matter. Store the samples in cold at 4ºC but it is not convenient to store them more than 28 days.

Bibliographical source of "*Chemical Oxigen Demand*. CHEMetrics. Water Analysis systems" **(14)**

## 4.2 Summary of tannery effluent treatment processes

In the following table there is a summary of the possible and usual treatments of wastewater from the tanning industry.

Table 2: wastewater treatments

| Treatment Stage | Function | Benefits |
|---|---|---|
| **Primary treatment** | | |
| Screening | To remove large part icles ofsuspended solids | Reduces COD andsuspended solids in effluent |
| Fat traps | To reduce fats, oils | Reduces fats and oils in effluent |
| **Pretreatments** | | |
| Lime presettling | To remove large quantities of suspended solids onsisting of pulped hair and undissolved lime | Improves sulphide oxidation andlowers catalyst requirement |
| Sulphide oxidation | To reduce sulphide content | Minimises odour nuisance and improves aerobic biologicalprocess |
| Chrome precipitation | Removes chromium from waste water | Allows final effluen t and othersludges to meets discharge and disposal limits |
| **Secondary treatment** | | |
| Activated sludge | To break down soluble and suspended organic matter, $NH_3$-N and other constituents | Reduces pollution and discharge costs |
| Addition of phosphates to aerobic biological process | Improves breakdown of organics and process efficiency by ±30% | Reduces pollutants more efficiently |
| Secondary settling | Removes biomass from effluent for sludge return and reinoculation of fresh effluent with biomass | Allows effluent with minimalsuspended solids and COD/BOD for discharge |
| Chemical precipitation | Precipitates suspended solids | Reduces COD/BOD andsuspended solids |
| **Tertiary treatment** | | |
| Biofiltration using plastic media | Reduces further soluble and suspended solids, fats and COD | Pro duces a high quality final effluent with low COD/BOD |
| **Advanced treatment** | | |
| Ultrafiltration | Removes fine particles of suspended solids and soluble fats | Preparation for reverse osmosis |
| reverse osmosis | Removes total dissolved inorganic solids and salts (NaCl) | Preparation for reverse osmosis |
| **Sludge dewatering** | | |
| Drying beds | Dewaters sludges by drainage and evaporation | Reduces potential odour nuisance and transport costs to landfill |
| Centrifuges | Separates water from solids | Reduces potential odour nuisance and transport costs to landfill |
| Belt presses | Separates water from solids by pressure between porous cloth | Reduces potential odour nuisance and transport costs to landfill |
| Pressure filter | Separates water from solids by pressure between plates | Reduces potential odour nuisanceand transport costs to landfill |

*Bibliographical source of official document by SWARTS, C.D; JACKSON-MOSS, C; ROWSWELL,R.A, MPOFU, A.B. "Water and wastewater management in the tanning and leather finishing industry"* ***(12)***

# 5. Statistical study: analysis of variance (ANOVA)

During the experimental study of the project a multifactorial experiment and its respective statistical study is carried out through an analysis of variance.

Below is a brief explanation of this statistical method.

ANOVA (ANalysis Of VAriance) models are multivariate dependency analysis techniques, which are used to analyze data from designs with one or more qualitative independent variables (measured on nominal or ordinal scales) and a quantitative dependent variable (measured with an interval or ratio scale). In this context, independent variables are often called factors (and their different possible states or values are levels or treatments) and the dependent variable is known as response.

The ANOVA models allow, basically, to compare the average values taken by the dependent variable in *"J"* populations in which the levels of factors are different, in order to determine if there are significant differences according to these levels or if, on the contrary, the response in each population it is independent of the factor levels. It is, therefore, a parametric contrast that extends to the case of *"J"* populations the contrast of the equality of means between two independent populations.

ANOVA tries to determine if the levels of factors can lead to differences in the response in the different groups or populations, contrasting the equality of means of the dependent variable in these groups. To do this, it is based on the study of variance.

If two populations have the same mean and the same variance, the union of both will also have the same mean and the same variance as the originals. Therefore, it is reasonable to think that, if the population variance were estimated from samples from the two initial populations, a similar result would be obtained as if the estimate were made with the union of both samples.

However, if the two populations have different mean (but the same variance), combining them would change both the average of the new distribution and its variance. In this case, if the population variance was estimated from a sample taken from the initial populations, the result would be substantially different from an estimate made from the joint sample. The same would happen if we were talking about more than two populations.

This observation is the starting point of ANOVA, which allows comparing the means of several populations based on the study of their variances.

In order to apply this technique, the following prerequisites must be verified:

- Independence: the individuals studied must be independent of each other.

- Randomness: the samples or groups under study must have been obtained randomly.
- Normality: the samples or groups analyzed must follow a Normal distribution.
- Homocedasticity: there must be equality of variances in the samples or groups studied.

### 5.1 ANOVA of one factor

In this study will perform the analysis of variance taking into account a factor in each analysis of variance.

The analysis of the variance of a factor is used to compare the average value of a quantitative dependent variable in several groups, which are differentiated by the levels of the factor considered.

In this section, an unbalanced fixed effects model will be considered, in which, the sample sizes do not have to be the same.

If we denote by *"Y"* to the dependent variable; *"J"* the number of samples or groups considered (each corresponding to a different level of the factor); $n_1$, $n_2$,… $n_J$ to the sizes of each of the samples; $n = \sum_{J=1}^{J} n_j$ to the total sample size; and "$Y_{ij}$" to the value of the variable corresponding to the observation "i" of the sample "j".

Table 3: info ANOVA 1

| SAMPLE | OBSERVATION | TOTAL | AVERAGE |
|---|---|---|---|
| 1 | $Y_{11}\ Y_{21}\ \cdots\ Y_{i1}\ \cdots\ Y_{n_1 1}$ | $T_1$ | $\overline{Y}_1$ |
| 2 | $Y_{12}\ Y_{22}\ \cdots\ Y_{i2}\ \cdots\ Y_{n_2 2}$ | $T_2$ | $\overline{Y}_2$ |
| $\vdots$ | $\vdots\ \vdots\ \vdots\ \vdots\ \vdots\ \vdots$ | $\vdots$ | $\vdots$ |
| $j$ | $Y_{1j}\ Y_{2j}\ \cdots\ Y_{ij}\ \cdots\ Y_{n_j j}$ | $T_j$ | $\overline{Y}_j$ |
| $\vdots$ | $\vdots\ \vdots\ \vdots\ \vdots\ \vdots\ \vdots$ | $\vdots$ | $\vdots$ |
| $J$ | $Y_{1J}\ Y_{2J}\ \cdots\ Y_{iJ}\ \cdots\ Y_{n_J J}$ | $T_J$ | $\overline{Y}_J$ |
| | | $T = \sum_{j=1}^{J} T_j$ | $\overline{Y} = \frac{T}{n}$ |

The application of the ANOVA technique is based on a hypothesis test. The null hypothesis that is contrasted in the one-way ANOVA is that the population means are equal:

H0: µ1 = µ2 = … = µJ

H1: in the opposite case

If the null hypothesis is accepted, it will mean that the groups do not differ in the average value of the dependent variable and that, consequently, said average value may be considered independent of the factor.

To test this hypothesis, we introduce the concepts of inter-group quadratic mean ($CM_E$) and intra-group quadratic mean ($CM_D$), which are given, respectively, by the expressions:

Table 4: info ANOVA 2

$$CM_E = \frac{\sum_{j=1}^{J} n_j \left(\overline{Y}_j - \overline{Y}\right)^2}{J-1} \quad \text{y} \quad CM_D = \frac{\sum_{j=1}^{J}\sum_{i=1}^{n_j} \left(Y_{ij} - \overline{Y}_j\right)^2}{n-J}.$$

The test statistic used by ANOVA to contrast the proposed null hypothesis is constructed from the previous concepts: specifically it is given by:

Table 5: info ANOVA 3

$$F_{J-1,n-J} = \frac{CM_E}{CM_D} = \frac{\dfrac{\sum_{j=1}^{J} n_j \left(\overline{Y}_j - \overline{Y}\right)^2}{J-1}}{\dfrac{\sum_{j=1}^{J}\sum_{i=1}^{n_j} \left(Y_{ij} - \overline{Y}_j\right)^2}{n-J}}.$$

Assuming a certain $H_0$, this statistic follows a F distribution of Snedecor with J-1 and n-J degrees of freedom; Therefore, given a level of significance α, the critical region will be determined by the values such that $F > F^{1-\alpha}_{J-1,n-J}$ and $P\left[F \leq F^{1-\alpha}_{J-1,n-J}\right] = 1 - \alpha$

A graphic study will help us to get an idea of the situation. Through the succession of Charts / Graphs Generator / Bars / Simple error bars commands and choosing the level of confidence in Element Properties, you arrive at the representation of confidence intervals for the average quotes in each sample.

However, graphic methods are not, in general, definitive. Therefore, in order to determine if there are differences and, if so, between which groups exist, it will be necessary to resort to the analysis of variance. To get to the ANOVA table, we must click Analyze / Compare means / ANOVA of a factor and then indicate the dependent variable and the factor.

All these statistical studies will be carried out with the **"Statgraphics XVII"** software.

*Blibliographical source of the study by ORDAZ, J; MELGAR, M; RUBIO, C. "Métodos estadísticos y econométricos en la empresa para finanzas" **(15)***

## 6. Appreciation of the look and feel of leather

In the experiments that are carried out apart from measuring pollution parameters such as the COD of different processes and chemicals used, the appearance of the leather will also be assessed.

After all, the assessment of the leather could be considered the most important part of the study, since the final objective of the processes and products is to obtain a good article. If for example you get very low water pollution values but the final article does not meet the expectations, the whole process will not help.

For this reason, one of the main reasons for choosing products and processes is the assessment and feel of the leather's appearance.

The parameters to measure these characteristics are totally subjective. Therefore, an internal valuation system was created.

This system consists of evaluating from 1 (very good) to 5 (very bad) 5 different parameters and in the end to average the result of all the parameters. This measurement is done by three technicians to make it more real and comparative.

The parameters to be measured are:

- **Break:** when folding the leather, the grain folds and separates from the corium. *(1 good break - 5 bad break)*

- **Fullness:** It is related to the break. It is a feeling of touch. Empty and hard skins have an unpleasant touch similar to cardboard and full and somewhat soft skins have a rubber-like feel. *(1 full leather - 5 empty)*

- **Grain softness:** Softness of the grain and what visual appearance it has. If the grain is fine and very marked. *(1 soft and fine grain - 5 rough grain and hard, marked, etc)*

- **Flesh softness:** The flesh side of the leather and its softness are valued. If the plush is soft or rough, it is hard and stuck or loose. *(1 flesh side is soft and nice plush touch - 5 plush stuck and hard)*

- **Color:** Visual assessment of how the color changes with respect to the original substrate. The original substrate has a rather white color and it is assessed whether this base color changes for example to brown in the case of vegetable extracts or to yellow due to the use of other products. *(1 white color - 5 other colors)*

The table for the assessments is as follows:

Tabla 6: Evaluation organoleptic parameters

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental X** | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

# EXPERIMENTAL STUDY

## Introduction

In this experimental part of the project it has been done a following application studies to get closer to the objective of seeing if it's possible to find processes with a good metal-free leather articles as a result and that the contamination of waste water will not be very high.

All tests are performed in the wet-end application laboratory in Trumpler Española S.A (TRESA).

This whole study is divided into several parts. From the first tests and the conclusion obtained a second experiment is proposed and so on until to get closer to the goal and design a final experimental process where conclusions can be drawn and a statistical analysis can be made.

Finally, one of the selected processes will be chosen and some leather will be prepared with this process as a final article.

## Material

**Laboratory drums:**

The laboratory drums are de main tool to perform the tests. They imitate the tanning process at an industrial level but in a laboratory.

The drums used are steel, you can control the temperature and the speed of rotation.

In the tests carried out used drums of three different sizes. The volume of the drum depends on the amount of leather that is going to work.

1) <u>Tandem of six small drums:</u>
   In these drums it has done the experimental 1 because the pieces of leather are small. These drums have a loading capacity of 1,5kgs each.


Fig 2: drums used experimental 1

2) <u>Four medium drums</u>

The dimension of these drums is bigger. Dimension (L*W*H) D600X300mm. In these drums the experimental studies 2,3 and four are carried out.

Fig 3: drums used in exp. 2, 3, 4 and 5

Fig 4: drums used for full hides

3) <u>Big drums.</u>

They only use these drums , that are bigger, when they work with full hides and don't cut the hides in some pieces.

Dimensions (L*W*H) 1950X1800X2000mm.

**Laboratory balance:**

They use laboratory balance to weight both chemicals and leathers. The precision of the balance is 0,01 grams.

**Chemical products:**

A wide variety of chemical products are used. The classification of them are: vegetable extracts, syntans, oils, resins, biopolymers, organic acids, dyes, surfactants, etc.

**Machinery for drying leather:**

The machinery that is used to dry the leather and give mechanical effect is the following:

- Setting machine (Bauce)
- Vacuum

- Toggling
- Streching/Staking machine
- Mill drum

**Chemical Oxigen Demand meter:**

Essential instrument for these studies that allows to measure the amount of oxygen demand in ppm, that there is in the baths (Kit Nanoclor DQO 15000 )

**pH meter:**

During the studies the pH of bath in controlled in many occasions.

**Physical testing equipment:**

To perform the physical tests of tensile strength and% elongation and tear resistance according to ISO standards, a dynamometer with its respective jaws is used.

- IUP 6 (EN ISO 3376): Tensile strength and % elongation.
- IUP 8 (EN ISO 3377-2): Tear load.

**Shrinkage temperature equipment:**

Instrument used to measure the shrinkage temperature of leather according to IUP 16 (EN ISO 3380) - Shrinkage temperature measurement up to 100 ° C.

**Fig 5: Equipment for measurement of shrinkage temperature.**

# 1. EXPERIMENTAL 1: *How some products of a different chemical nature affect the wet-white leather at the level of appearance/touch and contamination of waste water.*

In this first part of the study, they wanted to control the behavior of chemical products used in the processes of tanning, re-tanning and fatliquoring, to see the affinity with wet-white leather substrate. As these products are fixed on the leather, what aspect and touch they do, and the most important for the study, as contaminants are in the waste water at a level of chemical oxygen demand.

The wet-white substrate that we will use in all trials will be always the same. This leather is pre-tanned with aldehydes and resins intended for leather goods. This leather is metal-free. The thickness is 1.3 – 1.5 mm. It could also be used for upholstery, and even some articles of garment. In summary, it is a high-quality leather, with well beamhouse processes and that would be destined to rather soft articles, to understand, the opposite of a shoe upper. Even so it depends of tanning, re-tanning and fatliquoring it could reach many different items.

As the chemical nature of the products and the method of application are different in many cases, it is decided to classify the chemical products to be studied in four blocks.

Then it will be exposed the 4 blocks of products, their method of application and the results on shrinkage temperature, the COD value before and after fixing with formic acid, the pH, a subjective touch rating internally and valued by 3 people.

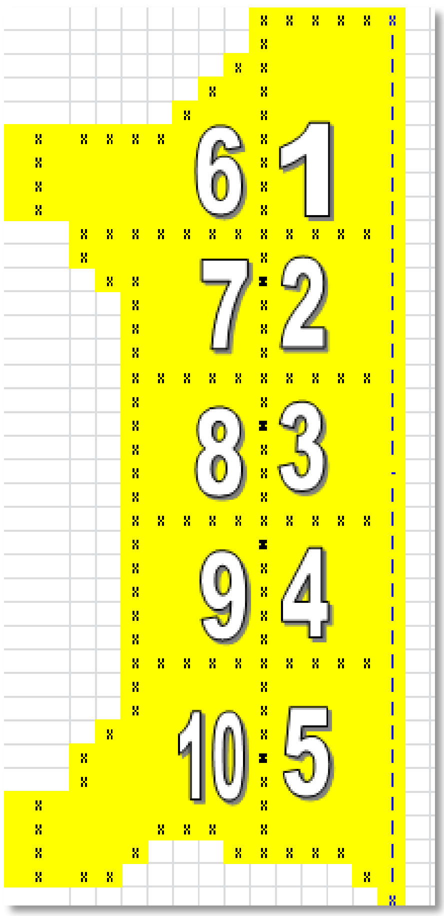
## 1.1 BLOCK 1: Vegetable extracts and syntans.

All products of this group can tan the leather. All of them have the power of tanning. They are:

**Table 7: products block 1**

| PRODUCT: | Description | % Active matter | pH (1:10) |
|---|---|---|---|
| 1) Mimosa | Vegetable extract. Powder | 100% | 3,9 |
| 2) Quebracho | Vegetable extract Powder | 100% | 4,4 |
| 3) Tara | Vegetable extract Powder | 100% | 3,7 |
| 4) Chestnut | Vegetable extract Powder | 100% | 3,0 |
| 5) Powder Syntan 1 | Acid syntan Brown Powder | 94% | 2,0 |
| 6) Powder Syntan 2. | Phenolic syntan. White powder | 95% | 4,0 |
| 7) Powder Syntan 3. | Condensation of sulfonic acid and aromatic sulfones. White powder | 95% | 4,0 |
| 8) Powder syntan 4 | Syntan condensed diphenyl. White poder. | 96% | 4,5 |
| 9) Liquid syntan 1 | Syntan modified naphtalensulfonic polymer. Yellow liquid. | 38% | 4.0 |
| 10) Liquid syntan 2. | Syntan condensed diphenyl. Yellow liquid. | 38% | 4.0 |

Division of leather:




The tanning / re-tanning process that is carried out is a very basic process. This first part of the process consists of wet-back the pre-tanned leather using a bit of moisturizing surfactant, oxalic acid and EDTA salt to eliminate possible stains and residues from the previous processes. A neutralized with sodium formate, a synthetic neutralizer and sodium bicarbonate is then carried out. The objective is to raise the pH around 5 because the tanning products that are studied have a better penetration and affinity with the anionic leather. Tanning is performed with each tanning product. The drums run 120 minutes and then the bath is increased and the temperature is raised to fix the product with formic acid that will use to lower the pH. A bath sample is collected before and after fixing in order to study the COD and the fixing capacity of each tanning product vary.

For the study, 15% (active matter) is applied of the tanning product.

Finally, in all the samples a standard fatliquoring is carried out with a sulphited natural / synthetic oil and an natural triglycerides and synthetic sulfated oil. The purpose of fatliquoring in this case is not to provide value, information about the study of waste water, it is intended that the leathers are greased and can compare the touch between them. If it didn't do the fatliquoring, the leathers would be very hard and firm and it would be very difficult to assess their appearance.

The drying of the leathers and the mechanical operations are the same for all samples.

| TARGET: | Bath exhaustion W.W leather: Block 1 (vegetables extracts and syntans) | | | | Date: 4/3/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30' | |
| Drain | | | | | |
| Wash | 200,0 | Water | 25º | 5' | |
| Drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40' | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60' | pH:5,2 |
| Drain | | | | | |
| Wash | 200,0 | Water | 25º | 5' | |
| Drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | X | VEG. EXTRACT / SYNTAN | | 120' | pH COD |
| | 100,0 | Water | 45º | | |
| | 1,5 | Formic acid (1:10) | | 30' | pH' COD' |
| Drain | | | | | |
| Wash | 200,0 | Water | 25º | 5' | |
| Drain | | | | | |
| | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **FATLIQUORING** | **150,0** | **Water** | **45º** | **5’** | |
| | **4,0** | **Sulphited natural/synthetic oil *4** | | | |
| | **3,0** | **Natural triglyceirds and sulphated synthetic *5** | | **90’** | |
| | **1,0** | **Formic acid** | | **30’** | |
| **drain** | | | | | |
| **wash** | **200,0** | **Water** | **25º** | **5’** | |
| **drain** | | | | | |
| | | | | | |
| **Mechanical Operations:** **Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7.** | | | | | |

Process 1: exp 1 block

## *RESULTS Block 1:*

COD results

**Table 8: COD results exp1 block1**

| PRODUCTS | weight (kg) | pH | pH' | bath 50% L | bath 50% COD mgO2/L | bath 50% COD mg O2/kg leather | bath 150% L | bath 150% COD' mgO2/L | bath 150% COD' mg O2/kg leather | Tg ºC |
|---|---|---|---|---|---|---|---|---|---|---|
| 1) Mimosa | 0,294 | 4,97 | 3,43 | 0,15 | 21840 | 10920 | 0,441 | 14900 | 22350 | 81 |
| 2) Quebracho | 0,289 | 5,22 | 3,56 | 0,14 | 23935 | 11968 | 0,434 | 12700 | 19050 | 79 |
| 3) Tara | 0,3 | 4,67 | 3,39 | 0,15 | 18705 | 9353 | 0,450 | 11340 | 17010 | 79 |
| 4) Chestnut | 0,257 | 4,81 | 3,49 | 0,13 | 39850 | 19925 | 0,386 | 17460 | 26190 | 79 |
| 5) Powder syntan 1 | 0,394 | 5,18 | 3,75 | 0,20 | 18560 | 9280 | 0,591 | 10500 | 15750 | 77 |
| 6) Powder syntan 2 | 0,456 | 5,20 | 3,91 | 0,23 | 17500 | 8750 | 0,684 | 9460 | 14190 | 79 |
| 7) Powder syntan 3 | 0,349 | 5,31 | 3,75 | 0,17 | 19066 | 9533 | 0,524 | 11400 | 17100 | 79 |
| 8) Powder syntan 4 | 0,365 | 4,90 | 3,49 | 0,18 | 35967 | 17984 | 0,548 | 13440 | 20160 | 79 |
| 9) Liquid syntan 1 | 0,373 | 4,49 | 3,69 | 0,19 | 34532 | 17266 | 0,560 | 15108 | 22662 | 85 |
| 10) Liquid syntan 2 | 0,356 | 4,50 | 3,74 | 0,18 | 25533 | 12767 | 0,534 | 17320 | 25980 | 83 |

## How COD values are calculated and expressed:

The bath is collected and the COD value is measured with the kit. The result is expressed directly in mg O2 / L bath. It is the first measure that can be seen in the table (next to the liters). All the values of the products studied are from the same amount of bath and therefore this expressed value is comparative between them.

Next, there is another way to express COD results. This way expresses the mg O2 / kg of leather. This way of expressing the results is used to eliminate possible differences in bath quantities and it is used to know exactly the mg or grams or kg of O2 consumed per kg of wet-white leather.

The calculation that is made to pass the reading value (mg O2 / L bath) to it (mg O2 / kg leather):

$$Lecture\ value\,\frac{mg\ O2}{L\ bath} \times \frac{(weight\ kg\ \times \%bath)L\ bath}{weight\ kg} = \frac{mg\ O2}{kg\ leather}$$

Example with the first sample of the table (mimosa):

$$21840\,\frac{mg\ O2}{L\ bath} \times \frac{(0{,}294 \times 0{,}5)L\ bath}{0{,}294\ kg} = 10920\,\frac{mg\ O2}{kg\ leather}$$

### Organoleptic assessment:

Table 9: Organoleptic evaluation exp1 block1

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 1** | | | | | | |
| Block 1 | | | | | | |
| 1) Mimosa | 1 | 2 | 1 | 1,5 | 5 | 2,1 |
| 2) Quebracho | 1,5 | 2 | 1,5 | 1,5 | 5 | 2,3 |
| 3) Tara | 1,5 | 2 | 1,5 | 1,5 | 3 | 1,9 |
| 4) Chestnut | 1,5 | 1 | 1,5 | 1,5 | 5 | 2,1 |
| 5)Powder syntan 1 | 1 | 2 | 2,5 | 3 | 2 | 2,1 |
| 6) Powder syntan 2 | 1 | 2,5 | 2,5 | 2 | 1,5 | 1,9 |
| 7) Powder syntan 3 | 1 | 2,5 | 2,5 | 1,5 | 1,5 | 1,8 |
| 8) Powder syntan 4 | 1 | 3 | 1,5 | 1,5 | 1 | 1,6 |
| 9) Liquid syntan 1 | 1 | 3 | 1,5 | 1,5 | 1,5 | 1,6 |
| 10) Liquid syntan 2 | 1 | 2 | 2 | 1,5 | 1 | 1,5 |

## *Discussion:*

In general, the highest COD values in the two measures are obtained by vegetable extracts. Powder syntans have lower bath exhaustion values although the shrinkage temperature is a bit lower.

The syntan with better bath exhaustion is the syntan powder 2 (9460 ppm in the fixation). Tare is the vegetable extract with lower values (11340 ppm in fixation). It highlights the liquid syntan 1 that has the highest shrinkage temperature (T 85ºC).

Organoleptic assessment presents similar values. The truth is that all products have given the leather good fullness characteristics. The problem with vegetable extracts is that they change the color of the leather a lot while the syntans keep it or even clarify it. By touch, the ones that have liked the most have been liquid syntans.

## *Conclusions:*

- <u>Better results of COD:</u> powdered syntans. Specifically the syntan powder 2 (phenolic syntan).

-<u>More tanning power:</u> plant extracts and liquid syntans.

- <u>Better organoleptic assessment</u>: liquid syntans.

## 1.2 BLOCK 2: Resins

Table 9: resins products

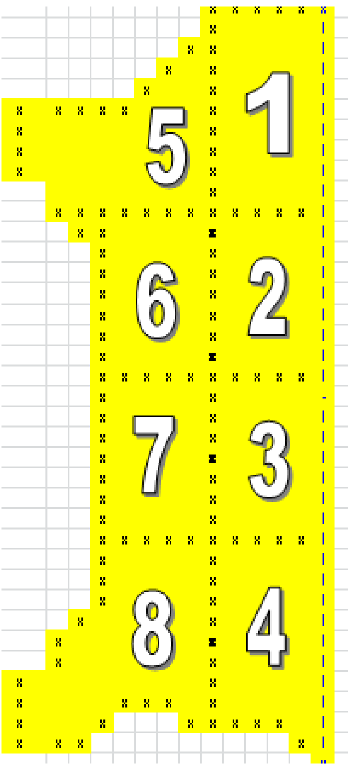
| PRODUCT: | Description | % Active matter | pH (1:10) |
|---|---|---|---|
| 1) Acrylic 1 | Acrylic polymer. Viscous liquid. | 30% | 5,0 |
| 2) Acrylic 2 | Polyacrylic polymer. Viscous liquid. | 33% | 3,5 |
| 3) Acrylic 3 | Modified metacrylic polymer. Viscous liquid. | 30% | 3,0 |
| 4) Acrylic 4 | Acrylic polymer. Viscous liquid. | 28% | 4,2 |
| 5) Acrylic 5 | Acrylic polymer. Viscous liquid. | 28% | 7,0 |
| 6) Styrene-maleic 1 | Styrene-maleic polymer. Viscous liquid | 25% | 5,5 |
| 7) Filler | Filler polysaccharides. White powder. | 95% | 7,0 |
| 8) Styrene- maleic 2 | Styrene maleic copolymer. Viscous liquid | 34% | 8,5 |

Here there is the range of resin products chosen for this study: five different acrylic resins, each one with a different pHs and a very different leather behavior in terms of touch. There are also two styrene maleic polymers and one filler. All products are viscous liquids minus the filler that is a white powder.

**6% active matter** of resin is applied in the process. The active matter of all resins is around 30%. They are liquid products.

The method of application and process is the same as in Block 1.

Division of leather:



| TARGET: | Bath exhaustion W.W leather: Block 2 (Resins) | | | Date: | 11/3/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| Drain | | | | | |
| Wash | 200,0 | Water | 25º | 5’ | |
| Drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| Drain | | | | | |
| Wash | 200,0 | Water | 25º | 5’ | |
| Drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | X | RESIN | | 120’ | pH COD |
| | 100,0 | Water | 45º | | |
| | 1,5 | Formic acid (1:10) | | 30’ | pH’ COD’ |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| Drain | | | | | |
| | | | | | |
| FATLIQUORING | 150,0 | Water | 45º | 5’ | |
| | 4,0 | Sulphited natural/synthetic oil *4 | | | |
| | 3,0 | Natural triglyceirds and sulphated synthetic *5 | | 90’ | |
| | 1,0 | Formic acid | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |

<u>Mechanical Operations:</u>
Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7.

Process 2 exp1 block

## *RESULTS Block 2:*

COD results

**Table 10: COD results block2**

| PRODUCTS | weight (kg) | pH | pH' | bath 50% L | bath 50% COD mgO2/L | bath 50% COD mg O2/kg leather | bath 150% L | bath 150% COD' mgO2/L | bath 150% COD' mg O2/kg leather | Tg ºC |
|---|---|---|---|---|---|---|---|---|---|---|
| 1) Acrylic 1 | 0,344 | 4,98 | 4,13 | 0,17 | 26050 | 13025 | 0,52 | 7900 | 1402 | 73 |
| 2) Acrylic 2 | 0,266 | 4,37 | 3,46 | 0,13 | 30900 | 15450 | 0,40 | 3450 | 366 | 73 |
| 3) Acrylic 3 | 0,291 | 4,47 | 3,28 | 0,15 | 11940 | 5970 | 0,44 | 3270 | 415 | 83 |
| 4) Acrylic 4 | 0,287 | 4,56 | 3,77 | 0,14 | 33700 | 16850 | 0,43 | 15800 | 1952 | 71 |
| 5) Acrylic 5 | 0,398 | 6,23 | 4,8 | 0,20 | 35900 | 17950 | 0,60 | 19160 | 4553 | 72 |
| 6) Styrene-maleic 1 | 0,258 | 5,29 | 4,06 | 0,13 | 41700 | 20850 | 0,39 | 4420 | 441 | 75 |
| 7) Filler | 0,262 | 5,39 | 3,43 | 0,13 | 7180 | 3590 | 0,39 | 6130 | 631 | 75 |
| 8) Styrene-maleic 2 | 0,374 | 5,32 | 3,84 | 0,19 | 34150 | 17075 | 0,56 | 2538 | 533 | 73 |

## Organoleptic assessment:

**Table 11: organoleptic evaluation block2**

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 1** | | | | | | |
| <u>Block 2</u> | | | | | | |
| 1) Acrylic 1 | 1 | 2 | 3,5 | 4 | 2,5 | 2,6 |
| 2) Acrylic 2 | 1 | 2 | 3,5 | 4,5 | 2,5 | 2,7 |
| 3) Acrylic 3 | 1 | 2,5 | 1,5 | 1,5 | 1,5 | 1,6 |
| 4) Acrylic 4 | 1 | 2,5 | 3,5 | 2,5 | 2 | 2,3 |
| 5) Acrylic 5 | 1 | 2 | 3,5 | 4,5 | 2,5 | 2,7 |
| 6) Styrene-maleic 1 | 1 | 2,5 | 1,5 | 1,5 | 1,5 | 1,6 |
| 7) Filler | 1 | 2,5 | 3,5 | 3 | 2,5 | 2,5 |
| 8) Styrene-maleic 2 | 1 | 2,5 | 2 | 2,5 | 2 | 2 |

## *Discussion:*

The COD values are much lower than the values of the vegetables and syntans products of block 1. The resins have a different chemical structure than the products in block 1, they don’t have reactive groups that can be oxidized.. The function of the resins is not to tan the skin but they have a filling power and they are deposited between the emptiest areas of the skin. These products have no tanning power as we can see in the shrinking temperatures. There is only one very notable exception. *Acrylic resin 3* (methacrylic acid) does have an important tanning power. In addition, it is the resin with the highest fixation and with the lowest COD result (3450 ppm after formic fixation). The shrinkage temperature with this resin is 10 degrees higher than almost all others. After this is followed by styrene maleic 1 with a very similar COD values but instead doesn’t have the tanning power.

The organoleptic assessment coincidentally coincides that the two resins with better fixation on the wet-white are the ones that look better. The break is very correct in all cases and what makes the valuation vary more is the softness of the grain and the flesh.

## *Conclusions:*

- <u>Better results of COD:</u> Acrylic resin 3 (methacrylic acid) and styrene – maleic 1.

-<u>More tanning power:</u> Only one. Acrylic resin 3

- <u>Better organoleptic assessment</u>: Acrylic resin 3 (methacrylic acid) and styrene – maleic 1

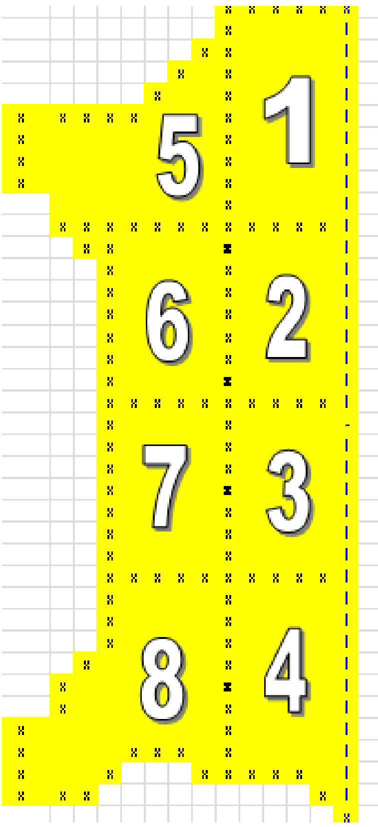
## 1.3 BLOCK 3: Biopolymers

Table 12: products block 3

| PRODUCT: | Description | % Active matter | pH (1:10) |
|---|---|---|---|
| 1) biopolymer powder 1 | Amphoteric natural biopolymer. Beige powder | 95% | 8,0 |
| 2) biopolymer powder 2 | Amphoteric natural biopolymer. Beige powder | 95% | 8,0 |
| 3) biopolymer powder 3 | Low molecular weight biopolymer. Beige powder. | 95% | 8,0 |
| 4) biopolymer powder 4 | Low molecular weight biopolymer. Beige powder. | 95% | 7,0 |
| 5) biopolymer liquid 1 | High molecular weight biopolymer. Yellow liquid. | 27% | 7,0 |
| 6) biopolymer liquid 2 | Low molecular weight biopolymer. Yellow viscous liquid. | 31% | 7,0 |
| 7) biopolymer liquid 3 | High molecular weight biopolymer. Yellow viscous liquid. | 28% | 4,0 |
| 8) blank – no product | | | |

We apply **15% of active matter**. The method of application and process is the same as in Block 1 and 2.

Division of leather:



| TARGET: | Bath exhaustion W.W leather: Block 3 (Biopolymers) | | | | Date: 18/3/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | X | BIOPOLYMER | | 120’ | pH COD |
| | 100,0 | Water | 45º | | |
| | 1,5 | Formic acid (1:10) | | 30’ | pH’ COD’ |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| Drain | | | | | |
| | | | | | |
| FATLIQUORING | 150,0 | Water | 45º | 5’ | |
| | 4,0 | Sulphited natural/synthetic oil *4 | | | |
| | 3,0 | Natural triglyceirds and sulphated synthetic *5 | | 90’ | |
| | 1,0 | Formic acid | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |

**Mechanical Operations:**
Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7.

Process: 3: exp1 block3

## *RESULTS Block 3:*

COD results

**Table 12: COD results exp1 block3**

| | | | | bath 50% | | | bath 150% | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| PRODUCTS | weight (kg) | pH | pH' | L | COD mgO2/L | COD mg O2/kg leather | L | COD' mgO2/L | COD' g O2/kg leather | Tg ºC |
| 1) Biopolymer powder 1 | 0,249 | 6,94 | 4,07 | 0,125 | 105600 | 52800 | 0,37 | 23980 | 35970 | 76 |
| 2) Biopolymer powder 2 | 0,247 | 6,08 | 3,86 | 0,124 | 55200 | 27600 | 0,37 | 14020 | 21030 | 75 |
| 3) Biopolymer powder 3 | 0,265 | 5,94 | 3,96 | 0,133 | 73600 | 36800 | 0,40 | 11120 | 16680 | 76 |
| 4) Biopolymer powder 4 | 0,281 | 6,11 | 4,04 | 0,141 | 110600 | 55300 | 0,42 | 10200 | 15300 | 76 |
| 5) Biopolymer liquid 1 | 0,27 | 6,35 | 4,83 | 0,135 | 95000 | 47500 | 0,41 | 26220 | 39330 | 77 |
| 6) Biopolymer liquid 2 | 0,267 | 5,95 | 4,86 | 0,134 | 46200 | 23100 | 0,40 | 29820 | 44730 | 77 |
| 7) Biopolymer liquid 3 | 0,219 | 4,18 | 3,57 | 0,110 | 48650 | 24325 | 0,33 | 17980 | 26970 | 76 |
| 8) Blanck - no product | 0,267 | 5,15 | 3,2 | 0,134 | 288 | 144 | 0,40 | 24420 | 36630 | 72 |

## Organoleptic assessment:

**Tabla13: organoleptic evaluation block3**

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 1** | | | | | | |
| Block 3 | | | | | | |
| 1) Biopolymer powder 1 | 1 | 1,5 | 3 | 4 | 2 | 2,3 |
| 2) Biopolymer powder 2 | 1 | 1,5 | 3 | 4 | 2 | 2,3 |
| 3) Biopolymer powder 3 | 1 | 2,5 | 3 | 4 | 2 | 2,5 |
| 4) Biopolymer powder 4 | 1 | 2 | 2 | 4 | 2 | 2,2 |
| 5) Biopolymer liquid 1 | 1 | 3 | 3 | 4 | 1,5 | 2,5 |
| 6) Biopolymer liquid 2 | 1 | 1,5 | 4 | 4,5 | 1,5 | 2,5 |
| 7) Biopolymer liquid 3 | 1 | 1,5 | 4 | 4,5 | 1,5 | 2,5 |
| 8) reference | 1 | 4 | 3 | 3 | 1 | 2,4 |

### *Discussion:*

These products are made from protein, organic raw material. For this reason COD values are higher than resins. The COD values are very high before fixing the products but it is true that after fixing with the formic they decrease greatly. They have very good fixing capacity. On this occasion it has the reference where no product has been applied. The shrinkage temperature of the reference sample is 72 ° C and the others range above 76 ° C. Biopolymers don't have a tanning affection but are more similar to resins and their function is to fill the skin and give a good appearance. The COD results are lower when it has been apply the protein powder, than if the biopolymer is liquid. It can highlight the powder biopolymer 4 which is the one that presents the best bath exhaustion, together with the powder biopolymer 3.

The organoleptic assessment of the leathers on this occasion is not very positive. It should be noted that these products are auxiliary and don't apply alone and with so much. For this reason, they are very well broken and full, but the softness of both, the grain and the flesh is very rough. An excess of product is noticed and the leather is very hard and has an unpleasant touch. Even so, it can highlight the powder biopolymer with little difference to others.

### *Conclusions:*

- Better results of COD: Biopolymer powder 3 and 4.

-More tanning power: -

- Better organoleptic assessment: Something better biopolymers powder.

## 1.4 BLOCK 4: Oils/Fatliquors.

Table 14: products block4

| PRODUCT: | Description | % Active matter | pH (1:10) |
|---|---|---|---|
| 1) Sulphited oil 1 | Natural/synthetic sulphited oil. Beige oil. | 43% | 7,5 |
| 2) Sulphited oil 2 | Natural sulphited oil. Brown oil. | 70% | 6,6 |
| 3) Sulphited oil 3 | Natural/synthetic sulphited oil. Brown oil. Red-brown oil. | 65% | 7,0 |
| 4) Sulphited oil 4 | Natural (fish) sulphited oil. Brown- red oil. | 90% | 6,5 |
| 5) Sulphited oil 5 | Sulphited and phosphate triglycerides and non-ionic surfactants. Red-brown oil. | 93% | 7,0 |
| 6) Sulphated oil 1 | Natural/synthetic sulphated oil. Brown-yellow oil. | 65% | 7,0 |
| 7) Sulphated oil 2 | Natural triglycerides and synthetic additives sulphated. Brown-yellow oil. | 75% | 7,2 |
| 8) Sulphated oil 3 ( | Natural triglycerides sulphated. Brown oil. | 55% | 7,0 |
| 9) Sulphated and sulphochlorinated oil | Synthetic sulphated and sulphoclorinated oil. Brown-yellow oil. | 67% | 7,3 |
| 10) Phosphoric ester oil | Synthetic phosphoric ester oil. Yellow oil. | 76% | 6,8 |
| 11) Phosphoric ester oil 2 | Phosphoric ester and synthetic fats oil. White oil. | 45% | 7,0 |
| 12)Polymer and silicone oil 1. | Waterproof oil. Yellow oil. | 58% | 8,0 |
| 13)Polymer and silicone oil 2. | Waterproof oil. Yellow oil. | 58% | 8,0 |
| 14)Polymer and silicone oil 3. | Waterproof oil. Yellow oil. | 56% | 8,0 |
| 15)Polymer and silicone oil 4. | Waterproof oil. Yellow oil. | 60% | 7,0 |
| 16) Lecithin ( | Natural vegetable oils and non-ionic emulsifiers. Brown oil. | 97% | 6,5 |
| 17) Phospholipid and synthetic oil | Natural phospholipids and synthetic oil. Brown viscous oil. | 50% | 7,5 |
| 18) Lanoline and lecithin | Natural oils and emulsifiable synthetic | 57% | 7,5 |

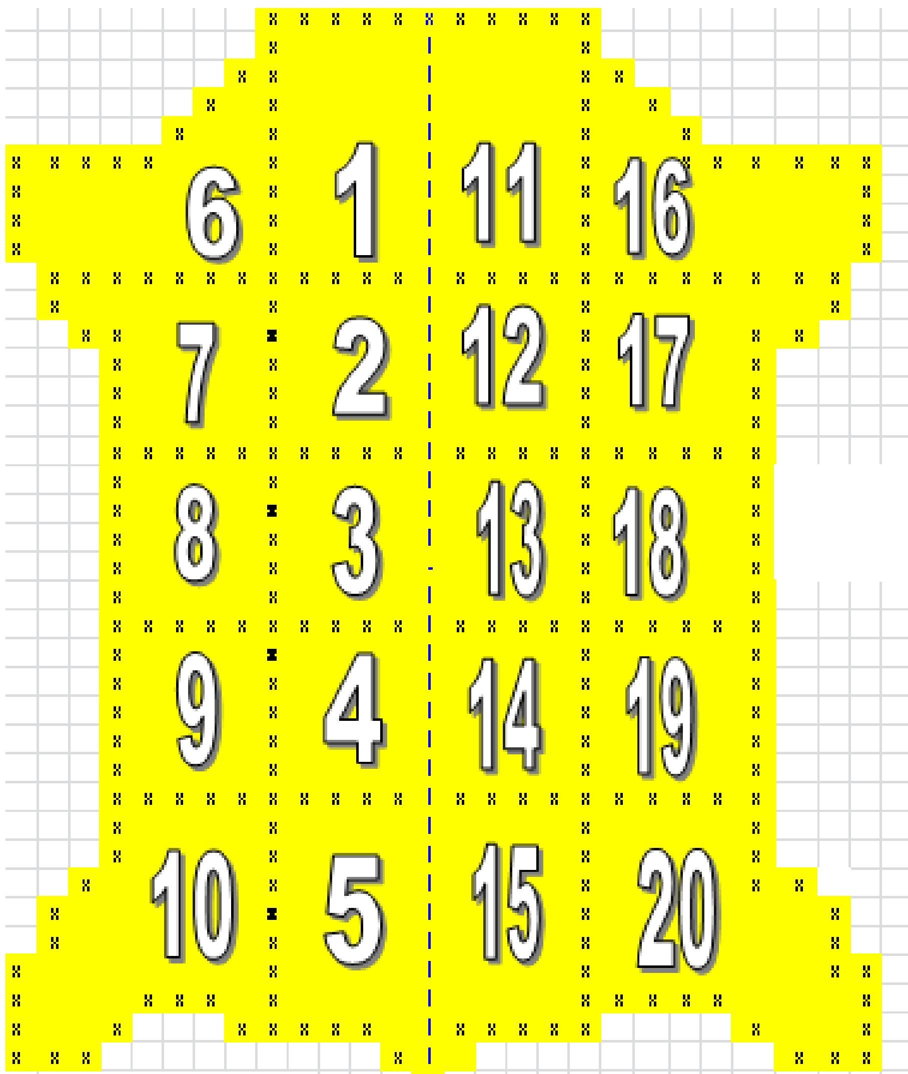
| | | | |
|---|---|---|---|
| | waxes. Brown very viscous oil. | | |
| 19) Polymer oil | Polymeric fatliquor. White oil. | 60% | 8,0 |
| 20) Cationic oil | Cationic fatliquor. White viscous oil. | 48% | 5,5 |

The method of applying oils is different from the method of blocks 1, 2, 3. Fatliquors don't apply like tanning or re-tanning products. They are applied with temperature and with a long bath normally after tanning / re-tanning. For this reason the application is different from the previous applications.

First the same tanning / re-tanning are performed for all samples. The products are fixed with formic acid but without lowering the pH so much, around 4. The bath is drained and a wash is performed.

The oils are then applied with 100% water and 6% active grease and the temperature inside the drum has to be around 45ºC. Depending on the active matter of each greasing, more or less actual amount will be applied. Finally the fixation is with 1% formic acid. A bath sample is collected to measure at the COD before and after fixing the fatliquor.

Division of leather:



| TARGET: | Bath exhaustion W.W leather: Block 4 (Oils) | | | | Date: 25/3/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 10,0 | Syntan naphtalensulphonic polymer (liquid) *6 | | 120’ | |
| | 5,0 | Syntan condensed diphenyl (powder) *7 | | | |
| | 100,0 | Water | 45º | | |
| | 0,5 | Formic acid (1:10) | | 30’ | pH: 3,8 – 4,0 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| Drain | | | | | |
| FATLIQUORING | 100,0 | Water | 45º | 5’ | |
| | X | Oil (Fatliquor) | | 90’ | COD pH |
| | 1,0 | Formic acid | | 30’ | COD’ pH’ |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| Mechanical Operations: Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7. | | | | | |

Process: 4: exp1 block4

## *RESULTS Block 4*

COD results

Table 15: COD results block4

| PRODUCTS | weight (kg) | pH | pH' | L | bath 100% COD mgO2/L | COD mg O2/kg leather | COD' mgO2/L | COD' g O2/kg leather | Tg ºC |
|---|---|---|---|---|---|---|---|---|---|
| 1) Sulphited oil 1 | 0,433 | 4,44 | 3,45 | 0,433 | 38200 | 38200 | 11540 | 11540 | 82 |
| 2) Sulphited oil 2 | 0,275 | 4,44 | 3,42 | 0,275 | 59400 | 59400 | 11860 | 11860 | 81 |
| 3) Sulphited oil 3 | 0,270 | 4,43 | 3,39 | 0,270 | 56600 | 56600 | 9960 | 9960 | 81 |
| 4) Sulphited oil 4 | 0,242 | 4,47 | 3,47 | 0,242 | 63200 | 63200 | 5220 | 5220 | 81 |
| 5) Sulphited oil 5 | 0,353 | 4,43 | 3,37 | 0,353 | 53250 | 53250 | 9440 | 9440 | 82 |
| 6) Sulphated oil 1 | 0,405 | 4,45 | 3,46 | 0,405 | 62750 | 62750 | 8200 | 8200 | 81 |
| 7) Sulphated oil 2 | 0,355 | 4,47 | 3,48 | 0,355 | 16650 | 16650 | 4360 | 4360 | 81 |
| 8) Sulphated oil 3 | 0,298 | 4,57 | 3,46 | 0,298 | 37950 | 37950 | 8580 | 8580 | 81 |
| 9) Sulphated / sulphochlarinated oil | 0,311 | 4,44 | 3,44 | 0,311 | 56500 | 56500 | 6580 | 6580 | 81 |
| 10) Phosphoric ester oil 1 | 0,525 | 4,61 | 3,45 | 0,525 | 82200 | 82200 | 9640 | 9640 | 81 |
| 11) Phosphoric ester oil 2 | 0,267 | 4,45 | 3,35 | 0,267 | 61450 | 61450 | 38100 | 38100 | 82 |
| 12) Polymer silicone oil 1 | 0,227 | 4,92 | 3,63 | 0,227 | 62150 | 62150 | 12140 | 12140 | 81 |
| 13) Polymer silicone oil 2 | 0,264 | 4,92 | 3,78 | 0,264 | 67050 | 67050 | 14500 | 14500 | 82 |
| 14) Polymer silicone oil 3 | 0,258 | 5,01 | 3,77 | 0,258 | 83400 | 83400 | 15740 | 15740 | 81 |
| 15) Polymer silicone oil 4 | 0,402 | 4,64 | 3,43 | 0,402 | 91900 | 91900 | 22600 | 22600 | 79 |
| 16) Lecithin | 0,402 | 4,44 | 3,4 | 0,402 | 44450 | 44450 | 8420 | 8420 | 81 |
| 17) Phospholipid and synthetic oil | 0,330 | 4,61 | 3,45 | 0,330 | 42350 | 42350 | 13900 | 13900 | 81 |
| 18) Lanoline and lecithin | 0,295 | 4,57 | 3,4 | 0,295 | 30550 | 30550 | 6680 | 6680 | 81 |
| 19) Polymer oil | 0,310 | 4,8 | 3,59 | 0,310 | 48600 | 48600 | 10980 | 10980 | 81 |
| 20) Cationic oil | 0,430 | 4,4 | 3,28 | 0,430 | 55100 | 55100 | 32100 | 32100 | 81 |

## Organoleptic assessment:

**Table 16: Organoleptic evaluation block4**

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 1** | | | | | | |
| Block 4 | | | | | | |
| 1) Sulphited oil 1 | 1 | 2 | 3 | 2 | 1,5 | 1,9 |
| 2) Sulphited oil 2 | 1 | 1,5 | 2,5 | 3,5 | 2 | 2,1 |
| 3) Sulphited oil 3 | 1 | 2,5 | 2,5 | 3,5 | 1,5 | 2,2 |
| 4) Sulphited oil 4 | 1 | 2 | 2 | 3 | 1,5 | 1,9 |
| 5) Sulphited oil 5 | 1 | 2 | 1,5 | 2 | 1,5 | 1,6 |
| 6) Sulphated oil 1 | 1 | 3,5 | 2,5 | 3 | 1,5 | 2,3 |
| 7) Sulphated oil 2 | 1 | 2 | 3 | 2 | 1,5 | 1,9 |
| 8) Sulphated oil 3 | 1 | 2,5 | 3 | 3,5 | 1,5 | 2,3 |
| 9) Sulphated sulphoclorinated | 1 | 3 | 2,5 | 3,5 | 1,5 | 2,3 |
| 10) Phosphoric ester oil 1 | 1 | 2,5 | 2,5 | 4 | 1,5 | 2,3 |
| 11) Phosphoric ester oil 2 | 1 | 2 | 3,5 | 4 | 2 | 2,5 |
| 12) W.P polymer silicone 1 | 1 | 2,5 | 1,5 | 2 | 1,5 | 1,7 |
| 13) W.P polymer silicone 2 | 1 | 2,5 | 1,5 | 2,5 | 1,5 | 1,8 |
| 14) W.P polymer silicone 3 | 1 | 2,5 | 1,5 | 2,5 | 1,5 | 1,8 |
| 15) W.P polymer silicone 4 | 1 | 2,5 | 2 | 3 | 1,5 | 2 |
| 16) Lecithin | 1 | 2,5 | 1,5 | 2 | 2 | 1,8 |
| 17) Phospholipid and synthetic | 1 | 3 | 1,5 | 2 | 2 | 1,9 |
| 18) Lanoline and lecithin | 1 | 2 | 1,5 | 2 | 2 | 1,7 |
| 19) Polymer oil | 1 | 3 | 2,5 | 2 | 1,5 | 2 |
| 20) Cationic oil | 1 | 2,5 | 3,5 | 3 | 2 | 2,4 |

### *Discussion:*

First note that fatliquorings have no tanning value. Even so, it was decided to measure the shrinkage temperature of each sample. All are around 82 ° C and this value that is not very high is thanks to the easy tanning / re-tanning and with a small amount of product that has been previously made in all the samples.

As for the COD results, it is very difficult to assess the results since practically every greasing even if it is from the same family has different values. In general, it can be said that all sulfated oils have low COD values if they are compare them with the other results. All results are below 10000ppm after fixation. This may indicate that this type of oils has a good affinity with the wet-white substrate. Sulphited oils are 3 of the 5 that have values below 10000ppm. One of the phosphoric esters has an acceptable value (9640ppm) and the other very high (38100ppm). Those that clearly don't have a good behavior in terms of fixation are silicone-based hydrophobic polymeric greases.

All values are very high. Lecithin and lanolin / lecithin present interesting COD results that could work.

In general it can say that each oil is manufactured in a different way and the raw materials if they are of vegetable or synthetic origin, the reactions, the emulsifiers used, make each one behave differently.

The organoleptic assessment cannot be grouped by fatliquor families. Each presents a different touch. In the conclusions there are the products that have liked the most in terms of appearance.

### *Conclusions:*

- <u>Better results of COD:</u> Considering COD values in ppm after fixation with formic acid.

1) Sulphated oil 2 (4360ppm)
2) Sulphited oil 4 (5220ppm)
3) Sulphated / sulphochlarinated oil (6580 ppm)
4) Lanoline / Lecithin (6680ppm)
5) Sulphated oil 1 (8200pmm)

-<u>More tanning power:</u> -

- <u>Better organoleptic assessment</u>:

1) Sulphited oil 5
2) W.P polymer silicone 1
3) Lanoline / Lecithin

## 2. EXPERIMENTAL 2: *Study of the selected products in a whole process of real wet-end for a possible commercial article.*

Experiment 2 is the continuation of experiment 1. The first part has served to know the products and to be able to select the best, in terms of bath exhaustion and leather appearance. In this second part the selected products will be applied but combined with each other in a real formula for a wet-white article.

4 different processes will be carried out. 2 of them are made with products that have given better COD results without taking into account the assessment of the appearance of the leather. One will be done with the fatliquoring in the same bath and the other with the fatliquoring in a separate bath.

The selected products with better exhaustion are:

- Syntan (Powder syntan 2)
- Resin (Acrylic 3)
- Biopolymer (Biopolymer powder 4)
- Fatliquoring (Sulphated oil 2 and sulphited oil 4)

On the other hand, the other two tests are carried out with the products that have given better results in the organoleptic evaluation without taking into account COD values. This doesn't mean that they have the worst COD results, but that this aspect has not been assessed. The process is also carried out with the fatliquoring in the same bath and in a separate bath.

The selected products are:

- Syntan (Liquid syntan 1)
- Resin (Acrylic 3)
- Biopolymer (Biopolymer powder 3)
- Fatliquoring (Sulphited oil 5 and lanoline / lecithin)

The tare extract is the vegetable tanning that will always be used. It has been chosen because it is the vegetable extract that has presented better fixation respect to the other extracts and that does not present such a considerable color change in the leather.

The objective of this second study is to observe if in a real process COD values vary greatly by selecting products that in experiment 1 have given lower values and another process with those that have not. Fatliquoring is also done in the same bathr or in a separate bath to see how it affects the exhaustion of the bath and the appearance of the leather. If the process works with the fatliquoring in the same bath you can save volume of contaminated water and process time.

| TARGET: | EXP. 2A: products with lower COD. Fatliquoring in different bath. | | | Date: | 1/4/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 7,0 | Tara extract | | | |
| | 7,0 | Powder syntan 2 (phenolic) | | 30’ | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 4 | | 15’ | |
| | 7,0 | Tara extract | | | |
| | 7,0 | Powder syntan 2 (phenolic) | | 20’ | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 4 | | 90’ | CODr:59600 ppm pH: 4,9 |
| | 100,0 | Water | 45º | | |
| | 1,5 | Formic acid (1:10) | | 30’ | CODr’ : 53200 ppm pH: 4,02 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| Drain | | | | | |
| | | | | | |
| FATLIQUORING | 100,0 | Water | 45º | 5’ | |
| | 8,0 | Sulphated oil 2 | | | |

| | | | | | |
|---|---|---|---|---|---|
| | 2,0 | Sulphited oil 4 (natural) | | 90’ | CODf: 21600ppm<br>pH: 3,96 |
| | 1,0 | Formic acid | | 30’ | CODf’: 13600<br>pH: 3,28 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| <u>Mechanical Operations:</u><br>Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7. | | | | | |

Process 5 exp2 lower COD / fat in bath apart

| TARGET: | EXP. 2A: products with lower COD. Fatliquoring in the same bath. | | | Date: | 1/4/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | Shaved weight | |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 7,0 | Tara extract | | | |
| | 7,0 | Powder syntan 2 (phenolic) | | 30’ | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 4 | | 15’ | |
| | 7,0 | Tara extract | | | |
| | 7,0 | Powder syntan 2 (phenolic) | | 20’ | |

| | | | | | |
|---|---|---|---|---|---|
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 4 | | 90’ | CODr:117000ppm pH: 4,44 |
| FATLIQUORING | 150,0 | Water | 45º | 5’ | |
| | 8,0 | Sulphated oil 2 | | | |
| | 2,0 | Sulphited oil 4 (natural) | | 90’ | CODf: 58800ppm pH: 4,73 |
| | 2,0 | Formic acid | | 30’ | CODf’: 43600ppm pH: 3,62 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| **Mechanical Operations:** Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7. | | | | | |

Process: 6 exp2 lower COD / fat in same bath

| TARGET: | EXP. 2B: products with best touch Fatliquoring in different bath. | | | Date: | 1/4/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | Shaved weight | |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 7,0 | Tara extract | | | |

| | | | | | |
|---|---|---|---|---|---|
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 30' | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 3 | | 15' | |
| | 7,0 | Tara extract | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 20' | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 3 | | 90' | CODr:58800 ppm pH: 4,6 |
| | 100,0 | Water | 45º | | |
| | 1,5 | Formic acid (1:10) | | 30' | CODr' : 46400 ppm pH: 3,95 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5' | |
| Drain | | | | | |
| | | | | | |
| FATLIQUORING | 100,0 | Water | 45º | 5' | |
| | 6,5 | Sulphited oil 5 | | | |
| | 3,5 | Lanoline and lecithin | | 90' | CODf: 32400ppm pH: 3,84 |
| | 1,0 | Formic acid | | 30' | CODf': 14400 ppm pH: 3,19 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5' | |
| drain | | | | | |
| | | | | | |

**Mechanical Operations:**
Horse up (overnight), setting-out, vacuum 2'/45ºC, hang dry, stake 6/7.

Process 7 exp2 best touch / fat in bath apart

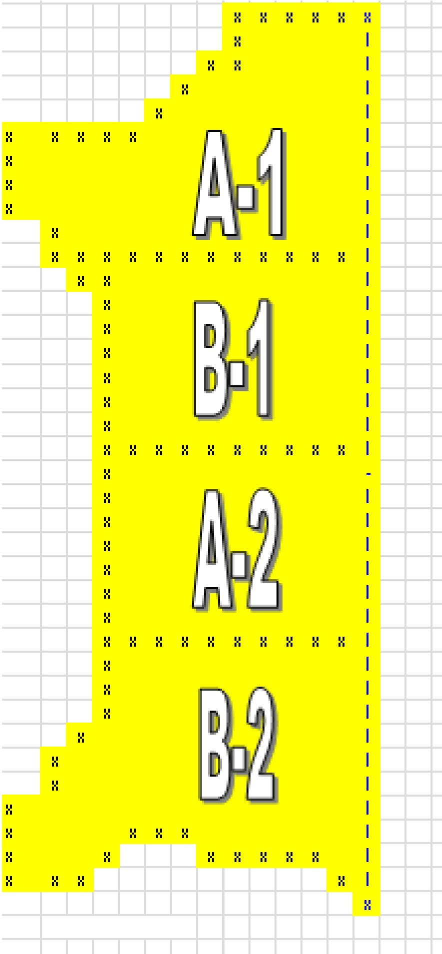
| | | | | | |
|---|---|---|---|---|---|
| TARGET: | EXP. 2B: products with best touch Fatliquoring in the same bath. | | | Date: | 1/4/2019 |
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30' | |

| | | | | | |
|---|---|---|---|---|---|
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 7,0 | Tara extract | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 30’ | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 3 | | 15’ | |
| | 7,0 | Tara extract | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 20’ | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 3 | | 90’ | CODr:73000 ppm pH: 4,44 |
| FATLIQUORING | 150,0 | Water | 45º | 5’ | |
| | 6,5 | Sulphited oil 5 | | | |
| | 3,5 | Lanoline and lecithin | | 90’ | CODf: 54800ppm pH: 4,38 |
| | 2,0 | Formic acid | | 30’ | CODf’: 45600 ppm pH: 3,62 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |

**Mechanical Operations:**
**Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7.**

Process: 8 exp2 best touch / fat in same bath

Division of leather:




### *RESULTS Exp 2*

COD results

Table 17: COD results exp2

**FATLIQUORING IN ANOTHER BATH**

| | A1 (best COD results) | | | B1 (best touch) | | |
|---|---|---|---|---|---|---|
| weight (kg): | | 0,933 | | | 0,607 | |
| | V (L) | mgO2/L bath | mg O2/kg leather | V (L) | mgO2/L bath | mg O2/kg leather |
| COD1 | | | | | | |
| bath 50% (tan/retan) | 0,467 | 59600 | 29800 | 0,304 | 73000 | 36500 |
| COD2 | | | | | | |
| bath 150% (fix retan) | 1,3995 | **53200** | **79800** | 0,911 | **46400** | **69600** |
| drain | | | | | | |
| COD3 | | | | | | |
| bath 100% (fatliquor) | 0,933 | 21600 | 21600 | 0,61 | 32400 | 32400 |
| COD4 | | | | | | |
| bath 100% (fix fatliquor) | 0,933 | **13600** | **13600** | 0,61 | **14400** | **14400** |
| drain | | | | | | |
| | | | | | | |
| ∑ COD drain water (mg O2/kg leather) : | | 93400,00 | | | 84000,00 | |
| ∑ Volume of waste water: | | 250% | | | 250% | |

**FATLIQUORING IN THE SAME BATH**

| | | A2 (best COD results) | | | B2 (best touch) | |
|---|---|---|---|---|---|---|
| weight (kg): | | 0,66 | | | 0,79 | |
| | V(L) | mgO2/L bath | mgO2/kg leather | V(L) | mgO2/L bath | mgO2/kg leather |
| COD1 | | | | | | |
| bath 50% (tan/retan) | 0,33 | 117000 | 58500 | 0,40 | 73000 | 36500 |
| COD2 | 1,32 | 58800 | 117600 | 1,58 | 54800 | 109600 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **bath 200% (fatliquor)** | | | | | | |
| **COD3** | | | | | | |
| **bath 200% (fix all)** | 1,32 | **43600** | **87200** | 1,58 | **45600** | **91200** |
| **drain** | | | | | | |
| | | | | | | |
| **∑ COD drain water (mg O2/kg leather) :** | | 87200 | | | 91200 | |
| **∑ Volume of waste water:** | | 200% | | | 200% | |

**Table18: organoleptic evaluation exp2**

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 2** | | | | | | |
| A1) fat in new bath | 1 | 1,5 | 1,5 | 2,5 | 2 | 1,7 |
| A2) fat in same bath | 1 | 1,5 | 1,5 | 2,5 | 2,5 | 1,8 |
| | | | | | | |
| B1) fat in new bath | 1 | 2 | 1 | 1 | 1,5 | 1,3 |
| B2) fat in same bath | 1 | 2 | 1 | 1 | 2 | 1,4 |

## *Discussion:*

The COD values of the process with the products that had given better depletion results and the COD values of the process with the products that looked better, the results are not very different. The difference can be considered minimal.

As to whether it is better to perform the greasing in the same bathroom or in the separate bathroom, the results indicate that it is more accurate both by volume of water consumed, time and absolute COD value, to perform the greasing in the same bathroom. This can be done as long as the greasing products are stable to the process since not changing the bathroom after tanning / re-tanning, it will have a lot of load of products of a different nature and could precipitate the fat or other defects appear.

If we analyze the appearance of the leather, it is considerably better using the products of process B. With the products of the process A fat does not penetrate well and is very much above. The combination of greases used in process A is not stable. In process B, on the other hand, the combination of the sulphited oil 5 and the lanolin / lecithin itself is stable to the process and gives leathers with a very positive organoleptic appearance.

## *Conclusions:*

- There is no considerable difference in COD using products that a priori by themselves have better values of fixation and bath exhaustion.

- If it is possible is better to do the fatliquoring in the same bath to reduce the volume of water used and save the intermediate washes, process time and above all the COD value is reduced in absolute value and a more ecological process can be achieved and much less polluting.

# *3.* EXPERIMENTAL 3: *Same process Wet-blue*

In this experiment the same process is carried out as experiment 2, the process that has been most liked with the products with the best appearance on the leather, but using a wet-blue instead of a wet-white as the raw material.

The objective of this study is to compare CODs using the same process.

It is true that in this case a good article with wet-blue leather is not sought since the process would have to be changed and different products and other quantities should be applied, but it will also be useful in terms of data on water pollution and to see how wet-blue fixes the products.

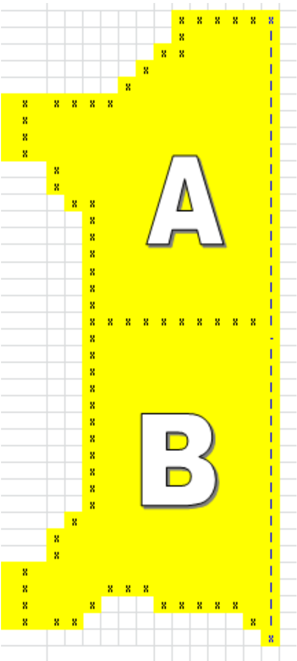
Two processes are performed to have more data to compare. One with the fatliquoring in the same bath and the other with the fatliquoring apart.

The products used are:

- Syntan (Liquid syntan 1)
- Resin (Acrylic 3)
- Biopolymer (Biopolymer powder 3)
- Fatliquoring (Sulphited oil 5 and lanoline / lecithin)

The methodology of the experiment is the same as in experiment 2.

Division of leather:



| TARGET: | EXP. 3: products with best touch in WB<br>A) Fatliquoring in different bath. | | | | Date: 8/4/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.B 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 7,0 | Tara extract | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 30’ | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 3 | | 15’ | |
| | 7,0 | Tara extract | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 20’ | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 3 | | 90’ | CODr:81000 ppm pH: 4,33 |
| | 100,0 | Water | 45º | | |
| | 1,5 | Formic acid (1:10) | | 30’ | CODr’ : 55000 ppm pH: 3,76 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| Drain | | | | | |
| | | | | | |
| FATLIQUORING | 100,0 | Water | 45º | 5’ | |
| | 6,5 | Sulphited oil 5 | | | |
| | 3,5 | Lanoline and lecithin | | 90’ | CODf: 20400ppm |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | pH: 3,30 |
| | 1,0 | Formic acid | | 30' | CODf': 14400 ppm<br>pH: 2,8 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5' | |
| drain | | | | | |
| | | | | | |
| **Mechanical Operations:**<br>Horse up (overnight), setting-out, vacuum 2'/45ºC, hang dry, stake 6/7. | | | | | |

Process 9: exp3 WB / fat in bath apart

| TARGET: | EXP. 3: products with best touch in WB<br>B) Fatliquoring in the same bath. | | | Date: | 8/4/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.B 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30' | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5' | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40' | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60' | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5' | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 7,0 | Tara extract | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 30' | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |
| | 5,0 | Biopolymer powder 3 | | 15' | |
| | 7,0 | Tara extract | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 20' | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | |

| | | | | | |
|---|---|---|---|---|---|
| | 5,0 | Biopolymer powder 3 | | 90’ | CODr:87000 ppm pH: 4,34 |
| FATLIQUORING | 150,0 | Water | 45º | 5’ | |
| | 6,5 | Sulphited oil 5 | | | |
| | 3,5 | Lanoline and lecithin | | 90’ | CODf: 49000ppm pH: 4,1 |
| | 2,0 | Formic acid | | 30’ | CODf’: 49000 ppm pH: 3,35 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| **Mechanical Operations:** Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7. | | | | | |

Process: 10: exp3 WB / fat in same bath

## *RESULTS Exp 3*

COD RESULTS

Tabla 7 COD results exp3

**FATLIQUORING IN ANOTHER BATH**

| | WET-BLUE exp3 | | | WET-WHITE exp2 | | |
|---|---|---|---|---|---|---|
| weight (kg): | | 1,65 | | | 0,607 | |
| | V (L) | mgO2/L bath | g O2/kg leather | V (L) | mgO2/L bath | mg O2/kg leather |
| COD1 | | | | | | |
| bath 50% (tan/retan) | 0,825 | 81000 | 40500 | 0,304 | 73000 | 36500 |
| COD2 | | | | | | |
| bath 150% (fix retan) | 2,475 | **55000** | **82500** | 0,911 | **46400** | **69600** |
| drain | | | | | | |
| COD3 | | | | | | |
| bath 100% (fatliquor) | 1,65 | 20400 | 20400 | 0,61 | 32400 | 32400 |
| COD4 | | | | | | |
| bath 100% (fix fatliquor) | 1,65 | **14400** | **14400** | 0,61 | **14400** | **14400** |
| drain | | | | | | |
| | | | | | | |
| ∑ COD drain water (mg O2/kg leather) : | | 96900,00 | | | 84000,00 | |
| ∑ Volume of waste water: | | 250% | | | 250% | |

**FATLIQUORING IN THE SAME BATH**

| | WET-BLUE exp3 | | | WET-WHITE exp2 | | |
|---|---|---|---|---|---|---|
| weight (kg): | | 1,6 | | | 0,79 | |
| | V (L) | mgO2/L bath | mgO2/kg leather | V(L) | mgO2/L bath | mgO2/kg leather |

| | | | | | | |
|---|---|---|---|---|---|---|
| **COD1** | | | | | | |
| **bath 50% (tan/retan)** | **0,8** | 87000 | 43500 | 0,40 | 73000 | 36500 |
| **COD2** | | | | | | |
| **bath 200% (fatliquor)** | **3,2** | 49000 | 98000 | 1,58 | 54800 | 109600 |
| **COD3** | | | | | | |
| **bath 200% (fix all)** | **3,2** | 49000 | **98000** | 1,58 | **45600** | **91200** |
| **drain** | | | | | | |
| | | | | | | |
| **∑ COD drain water (mg O2/kg leather) :** | | 98000 | | | 91200 | |
| **∑ Volume of waste water:** | | 200% | | | 200% | |

**Table 8: Organoleptic evaluation exp3**

Organoleptic assessment:

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 3** | | | | | | |
| A) Fat in new bath | 2 | 2,5 | 2 | 2 | | 1,35 |
| B) Fat in same bath | 2 | 2,5 | 2 | 2 | | 1,375 |

### *Discussion:*

As can be seen in the COD results, there is practically no different when using wet-blue with wet-white. Even the results are a little better using the wet-white.

This doesn't mean that it is so in all the processes that are carried out. But with this process, using these products, the results of bath exhaustion and product fixation are better with the wet-white substrate.

### *Conclusions:*

It is common to hear that the polluting load of baths in wet-white processes is greater than using wet-blue. This experiment has shown that it doesn't have to be this way and that not the same happens in all processes. Of course, it is true that the cationic chrome tanning with the anionic products in the re-tanning may have a greater fixation with a low pH but not in all cases the same thing happens.

In this case, to carry out this specific article with this process, the processes fix better or equal with the wet-white than with the wet-blue.

# 4. EXPERIMENTAL 4: *The effect of resins to fix a low pH.*

In this experiment the same recipe and the same products as in the two previous experiments are still used. However there is a variant in the process. On this occasion it will be studied whether by applying different resins at the end of the process with the pH of the bath under fixation, COD can be decreased or at least not increased.

The hypothesis is that by applying the resins in acidic medium they will be quickly fixed on the leather due to their anionic nature and possibly they can drag organic products that are still in the bath and have not been fixed, reducing the final COD.

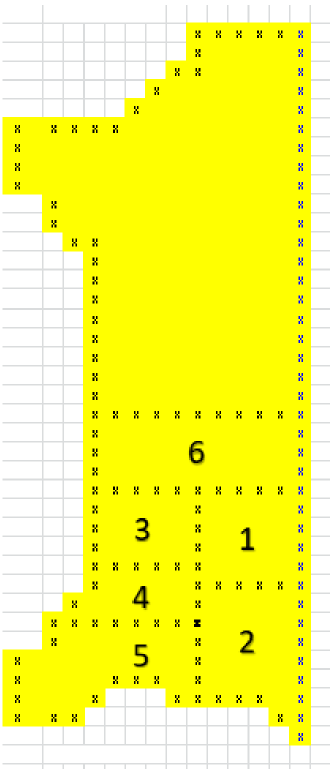
This time only one process is done with the greasing in the same bathroom.

The resins used for this experiment are:

1) Acrylic 3 (pH 3  30%) poliacrylic acids
2) Acrylic 2 (pH 3,5  33%) poliacrylic acids
3) Styrene – maleic 1 (pH 5,5 25%) styrene malein
4) Styrene-maleic 2 (pH 8,5  34%) styrene malein
5) Acrylic 1 (pH 5 30%) acrylic polymer

10% of each resin is applied. About 3% of active matter.

Division of leather:



| TARGET: | EXP. 4: the effect of resins to fix a low pH | | | | Date: | 13/4/2019 |
|---|---|---|---|---|---|---|
| Raw material: | Italian W.W pretanned 1.3-1.5 mm Tg 75ºC | | % based on: | | Shaved weight | |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) | |
| WET- BACK | 200,0 | Water | 30 º | | | |
| | 0,5 | Surfactant (wetting) *1 | | | | |
| | 0,3 | Oxalic acid | | | | |
| | 0,3 | E.D.T.A *2 | | 30' | | |
| drain | | | | | | |
| wash | 200,0 | Water | 25º | 5' | | |
| drain | | | | | | |
| | | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | | |
| | 1,0 | Sodium formate | | | | |
| | 1,0 | Neutralisation syntan *3 | | 40' | pH: 4,5 | |
| | 0,7 | Sodium bicarbonate | | 60' | pH:5,2 | |
| drain | | | | | | |
| wash | 200,0 | Water | 25º | 5' | | |
| drain | | | | | | |
| | | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | | |
| | 7,0 | Tara extract | | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 30' | | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | | |
| | 5,0 | Biopolymer powder 3 | | 15' | | |
| | 7,0 | Tara extract | | | | |
| | 18,0 | Liquid syntan 1 (naphtalensulphonic) | | 20' | | |
| | 5,0 | Acrylic 3 (methacrylic polymer) | | | | |
| | 5,0 | Biopolymer powder 3 | | 90' | | |
| FATLIQUORING | 150,0 | Water | 45º | 5' | | |
| | 6,5 | Sulphited oil 5 | | | | |
| | 3,5 | Lanoline and lecithin | | 90' | | |
| | 1,0 | Formic acid | | 20' | | |
| | 1,0 | Formic acid | | 20' | pH: 3,7 | |
| | 10,0 | Acrylic | | 40' | | |
| | 0,5 | Formic acid | | 20' | COD1,2,3,4,5,6 | |
| drain | | | | | | |
| wash | 200,0 | Water | 25º | 5' | | |
| drain | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | |

**Mechanical Operations:**
**Horse up (overnight), setting-out, vacuum 2'/45ºC, hang dry, stake 6/7.**

Process: 11: exp 4

## *RESULTS exp 4*

### COD RESULTS

Table 21: COD results exp4

| | | | bath 200% | | | |
|---|---|---|---|---|---|---|
| PRODUCTS | weight (kg) | pH' | V (L) | COD mgO2/L | COD mg O2/kg leather | Tg ºC |
| 1) Acrylic 3 | 0,311 | 3,74 | 0,622 | 48000 | 96000 | 86 |
| 2) Acrylic 2 | 0,32 | 3,77 | 0,64 | 53000 | 106000 | 86 |
| 3) Styrene - maleic 1 | 0,26 | 3,96 | 0,52 | 50000 | 100000 | 88 |
| 4) Styrene - maleic 2 | 0,3 | 3,97 | 0,6 | 45000 | 90000 | 86 |
| 5) Acrylic 1 | 0,38 | 3,89 | 0,76 | 53000 | 106000 | 85 |
| 6) Reference (no resin) | 0,51 | 3,78 | 1,02 | 52000 | 104000 | 86 |

### Organoleptic assesment:

Table 22: organoleptic evaluation exp4

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 4** | | | | | | |
| 1) Acrylic 3 | 1 | 2 | 1 | 1 | 2 | 1,4 |
| 2) Acrylic 2 | 1 | 2 | 2 | 2 | 2 | 1,8 |
| 3) Styrene-maleic 1 | 1 | 2 | 1,5 | 2 | 2 | 1,7 |
| 4) Syrene-maleic 2 | 1 | 2 | 1,5 | 1,5 | 2 | 1,6 |
| 5) Acrylic 1 | 1 | 2 | 1,5 | 2 | 2 | 1,7 |
| 6) reference (no resin) | 1 | 2 | 1,5 | 1,5 | 2 | 1,6 |

### *Discussion:*

The COD results indicate that when applying the resins in these process conditions, the COD values do not increase and even on some occasions decrease slightly, with respect to the reference where no resin has been applied.

As for the appearance of the leather, the article obtained is very good. It should be noted that the wet-white used on this occasion is a different one from the previous experiments. This is very positive because it indicates that this process is applicable not only to the substrate that was being worked on but with other wet-whites with different pre-tanning processes.

The reference sample looks very good but using some of the resins can be improved.

### *Conclusions:*

The resins that slightly reduce the COD with respect to the reference and that improve the final appearance of the leather are:

- Acrylic 3
- Styrene maleic 2

# 5. EXPERIMENTAL 5: *Final experimental - multifactorial study*

After performing all the previous experiments, the final multifactorial experiment is considered taking into account the results obtained in the previous tests.

The structure of the recipe is the same as in the previous processes. The fatliquoring will be done in the same bath.

So the experiment will have the following structure:

- 4 factors are considered in the experiment:

**Factor 1: Replacement syntan**

This factor will have two levels that will be two different syntans.

<u>Syntan 1</u>: Syntan liquid 1 (diphenylsulfone)

<u>Syntan 2</u>: Syntan Powder 2 (Phenolic)

In the recipe there will be one or the other and *15% in active matter* is applied.

**Factor 2: Resin**

2 levels

<u>Resin 1:</u> Acrylic 3 (methacrylic acid)

<u>Resin 2:</u> Maleic Styrene 2

In the recipe there will be one or the other. A total *of 6% of active matter* will be applied.

**Factor 3: Biopolymer**

2 levels

<u>Biopolymer 1:</u> Liquid biopolymer 3 (pH 4.0)

<u>Biopolymer 2:</u> Biopolymer powder 2 (pH 8.5)

In the recipe there will be either one or the other.

**Factor 4: Application method of fatliquoring.**

3 application levels.

The combination of oils that has worked best is selected, which is 8% in active matter of sulphited oil 5 and 2% in active matter of lanolin / lecithin.

The application methods are as follows:

<u>Fatliquoring application 1:</u>

1/3 part of oil in the re-tanning and 2/3 parts in the main fatliquoring.

<u>Fatliquoring application 2:</u>

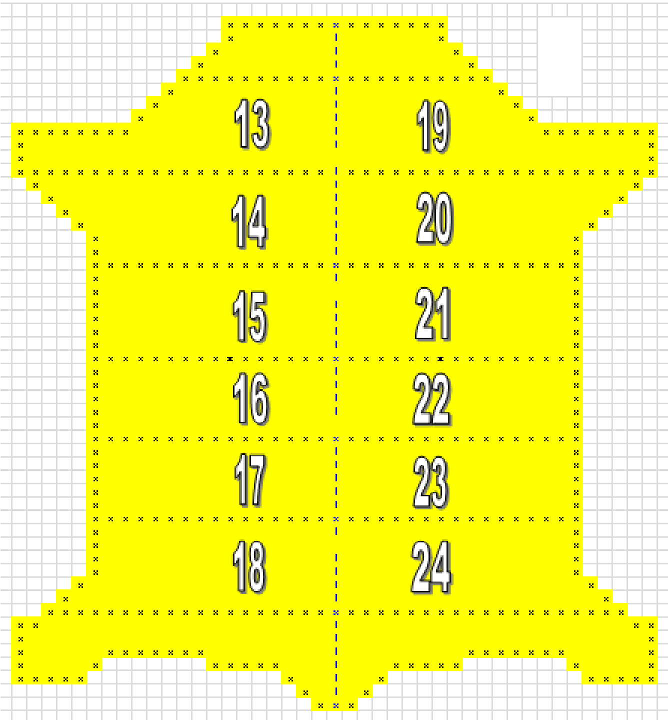
2/3 parts of oil in the re-tanning and 1/3 parts in the main fatliquoring.

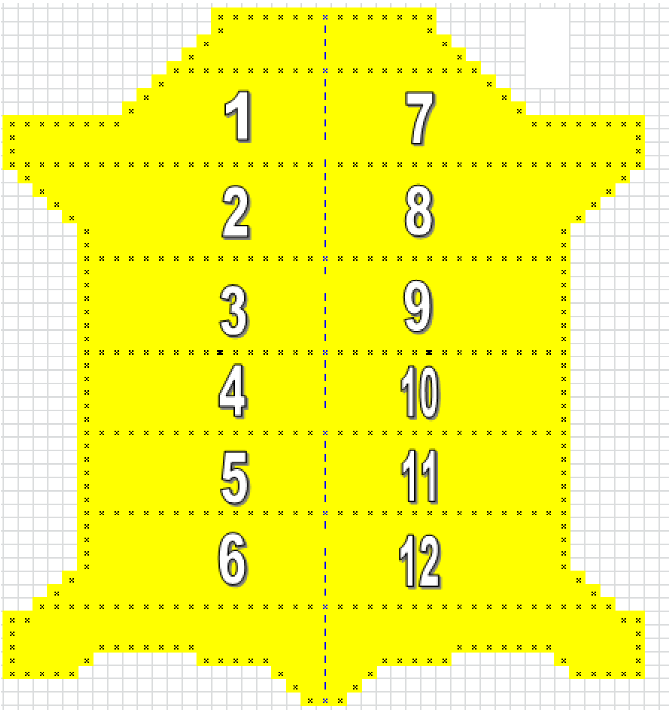
<u>Fatliquoring application 3:</u>

3/3 parts, all oil as main fatliquoring.

All these factors and levels are combined and the experiment has 24 different tests / combinations. At the end of the process the bath will be collected to measure the COD of each test.

Division of leather:



| TARGET: | EXP. 5: final experimental. | | | Date: | 16/4/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,3 | Oxalic acid | | | |
| | 0,3 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 100,0 | Water | 30º | | |
| | 1,0 | Sodium formate | | | |
| | 1,0 | Neutralisation syntan *3 | | 40’ | pH: 4,5 |
| | 0,7 | Sodium bicarbonate | | 60’ | pH:5,2 |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| TAN/RETAN | 50,0 | Water | 30º | | |
| | 7,5 | Tara extract | | | |
| | 7,5 | Replaced Syntan | | | |
| | 1,5 | Resin | | 60’ | |
| | 50,0 | Water | 40º | | |
| | X | Fatliquor | | 15’ | |
| | 7,5 | Tara extract | | | |
| | 7,5 | Replaced Syntan | | | |
| | 1,5 | Resin | | | |
| | 4,0 | Biopolymer | | 60’ | |
| FATLIQUORING | 100,0 | Water | 45º | 5’ | |
| | X | Fatliquor | | 90’ | |
| | 1,0 | Formic acid | | 20’ | |
| | 1,0 | Formic acid | | 20’ | pH: 3,7 |
| | 3,0 | Resin | | 40’ | |
| | 0,5 | Formic acid | | 20’ | COD final ¿? |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |

**<u>Mechanical Operations:</u>**
**Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7.**

Process: 12 multifactorial experiment

**% of products in active matter.**

The data is analyzed using a variance analysis table with the objective of studying whether the COD value is determined by a factor, or factors or the combination between them.

The physical appearance of the leather will also be assessed, as in all previous studies.

## *RESULTS exp 5*

### COD results

Table 23 experimental design and COD results

| | Replaced syntan (15% active matter) | | Resin (6% active matter) | | Biopolymer (4% active matter) | | 8% a.m sulfited natural/synthetic Sulphited oil 5 (pH 7,0 - 93% a.m) 2% a.m lecitine / lanoline Lanoline and lecithine (pH 7,5 - 57% a.m) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | diphenylsulfone (liquid) pH 4,0 (38% a.m) | phenolic (powder) pH 4,0 (95% a.m) | metacrylic pH 3,0 (30% ) | styrene malein pH 8,5 (34% ) | liquid pH 4,0 (25% a.m) | powder pH 8,5 (90% a.m) | | | | |
| TEST | Liquid Syntan 1 | Powder Syntan 2 | Acrylic 3 | Styrene maleic 2 | b.p liquid 3 | b.p powder 2 | 1/3 retan 2/3 fatliquor | 2/3 retan 1/3 fatliquor | 0/3 retan 3/3 fatliquor | COD ppm |
| 1 | X | | X | | X | | X | | | 67000 |
| 2 | X | | X | | X | | | X | | 74000 |
| 3 | X | | X | | X | | | | X | 69000 |
| 4 | X | | X | | | X | X | | | 64000 |
| 5 | X | | X | | | X | | X | | 60000 |
| 6 | X | | X | | | X | | | X | 65000 |
| 7 | X | | | X | X | | X | | | 64000 |
| 8 | X | | | X | X | | | X | | 57000 |
| 9 | X | | | X | X | | | | X | 65000 |
| 10 | X | | | X | | X | X | | | 55000 |
| 11 | X | | | X | | X | | X | | 63000 |
| 12 | X | | | X | | X | | | X | 66000 |
| 13 | | X | X | | X | | X | | | 42000 |
| 14 | | X | X | | X | | | X | | 53000 |
| 15 | | X | X | | X | | | | X | 54000 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 16 | | X | X | | | X | X | | | **48000** |
| 17 | | X | X | | | X | | X | | **47000** |
| 18 | | X | X | | | X | | | X | **55000** |
| 19 | | X | | X | X | | X | | | **51000** |
| 20 | | X | | X | X | | | X | | **53000** |
| 21 | | X | | X | X | | | | X | **51000** |
| 22 | | X | | X | | X | X | | | **47000** |
| 23 | | X | | X | | X | | X | | **49000** |
| 24 | | X | | X | | X | | | X | **42000** |

## Organoleptic assesment:

Table 24: organoleptic evaluation exp 5

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| **Experimental 5** | | | | | | |
| 1) | 1 | 1,5 | 1,5 | 1 | 2,5 | 1,5 |
| 2) | 1 | 1,5 | 1 | 1 | 2,5 | 1,4 |
| 3) | 1 | 1,5 | 1,5 | 1 | 2,5 | 1,5 |
| 4) | 1 | 1,5 | 1,5 | 1 | 2,5 | 1,5 |
| 5) | 1 | 1,5 | 1 | 1 | 2,5 | 1,4 |
| 6) | 1 | 1,5 | 1,5 | 1 | 2,5 | 1,5 |
| 7) | 1 | 1,5 | 2 | 1 | 2,5 | 1,6 |
| 8) | 1 | 1,5 | 1,5 | 1 | 2,5 | 1,5 |
| 9) | 1 | 1,5 | 2 | 1 | 2,5 | 1,6 |
| 10) | 1 | 1,5 | 2,5 | 1 | 2,5 | 1,7 |
| 11) | 1 | 1,5 | 2 | 1 | 2,5 | 1,6 |
| 12) | 1 | 2 | 2 | 1 | 2,5 | 1,7 |
| 13) | 1 | 2 | 1,5 | 1,5 | 2 | 1,6 |
| 14) | 1 | 2 | 1,5 | 1,5 | 2 | 1,6 |
| 15) | 1 | 2 | 1,5 | 1,5 | 2 | 1,6 |
| 16) | 1 | 2 | 2 | 1,5 | 2 | 1,7 |
| 17) | 1 | 2 | 1,5 | 1,5 | 2 | 1,6 |
| 18) | 1 | 2 | 2 | 1,5 | 2 | 1,7 |
| 19) | 1 | 2 | 2 | 2 | 2 | 1,8 |
| 20) | 1 | 2 | 2 | 2 | 2 | 1,8 |
| 21) | 1 | 2 | 2 | 2 | 2 | 1,8 |
| 22) | 1 | 2 | 1,5 | 2 | 2 | 1,7 |
| 23) | 1 | 2 | 1,5 | 2 | 2 | 1,7 |
| 24) | 1 | 2 | 1,5 | 2 | 2 | 1,7 |

### *Discussion:*

There are clear differences between the COD results. The analysis of variance (ANOVA) is then carried out.

It should be noted that by performing the analysis of variance with the 24 tests, there was one of the values that caused the results to be neglected. This is the COD value of sample 13. This value has been removed to perform the statistical study. A possible error in the process or in the COD measurement may have been the cause of this erroneous result.

| | SYNTAN | RESIN | BIOPOLYMER | FAT method | COD ppm (dependent variable) |
|---|---|---|---|---|---|
| 1 | 0 | 0 | 0 | -1 | 67000 |
| 2 | 0 | 0 | 0 | 0 | 74000 |
| 3 | 0 | 0 | 0 | 1 | 69000 |
| 4 | 0 | 0 | 1 | -1 | 64000 |
| 5 | 0 | 0 | 1 | 0 | 60000 |
| 6 | 0 | 0 | 1 | 1 | 65000 |
| 7 | 0 | 1 | 0 | -1 | 64000 |
| 8 | 0 | 1 | 0 | 0 | 57000 |
| 9 | 0 | 1 | 0 | 1 | 65000 |
| 10 | 0 | 1 | 1 | -1 | 55000 |
| 11 | 0 | 1 | 1 | 0 | 63000 |
| 12 | 0 | 1 | 1 | 1 | 66000 |
| 13 | 1 | 0 | 0 | 0 | 53000 |
| 14 | 1 | 0 | 0 | 1 | 54000 |
| 15 | 1 | 0 | 1 | -1 | 48000 |
| 16 | 1 | 0 | 1 | 0 | 47000 |
| 17 | 1 | 0 | 1 | 1 | 55000 |
| 18 | 1 | 1 | 0 | -1 | 51000 |
| 19 | 1 | 1 | 0 | 0 | 53000 |
| 20 | 1 | 1 | 0 | 1 | 51000 |
| 21 | 1 | 1 | 1 | -1 | 47000 |
| 22 | 1 | 1 | 1 | 0 | 49000 |
| 23 | 1 | 1 | 1 | 1 | 42000 |

Table 25: Data table ANOVA

## Results ANOVA:

**Table 26: summary results ANOVA**

**Table of Least Squares Means for COD with 95,0% Confidence Intervals**

| | | | *Stnd.* | *Lower* | *Upper* |
|---|---|---|---|---|---|
| *Level* | *Count* | *Mean* | *Error* | *Limit* | *Limit* |
| GRAND MEAN | 23 | 57178,2 | | | |
| Syntan | | | | | |
| 0 | 12 | 64083,3 | 1062,26 | 61842,2 | 66324,5 |
| 1 | 11 | 50273,1 | 1119,72 | 47910,7 | 52635,6 |
| Resin | | | | | |
| 0 | 11 | 59106,5 | 1119,72 | 56744,1 | 61468,9 |
| 1 | 12 | 55250,0 | 1062,26 | 53008,8 | 57491,2 |
| Biopolymer | | | | | |
| 0 | 11 | 59273,1 | 1119,72 | 56910,7 | 61635,6 |
| 1 | 12 | 55083,3 | 1062,26 | 52842,2 | 57324,5 |
| Fat method | | | | | |
| -1 | 8 | 58375,0 | 1301,0 | 55630,1 | 61119,9 |
| 0 | 8 | 57000,0 | 1301,0 | 54255,1 | 59744,9 |
| 1 | 7 | 56159,7 | 1405,24 | 53194,9 | 59124,5 |

**The StatAdvisor**
This table shows the mean COD for each level of the factors. It also shows the standard error of each mean, which is a measure of its sampling variability. The rightmost two columns show 95,0% confidence intervals for each of the means. You can display these means and intervals by selecting Means Plot from the list of Graphical Options.

**Analysis of Variance for COD - Type III Sums of Squares**

| *Source* | *Sum of Squares* | *Df* | *Mean Square* | *F-Ratio* | *P-Value* |
|---|---|---|---|---|---|
| MAIN EFFECTS | | | | | |
| A:Syntan | 1,0841E9 | 1 | 1,0841E9 | 80,06 | 0,0000 |
| B:Resin | 8,45381E7 | 1 | 8,45381E7 | 6,24 | 0,0230 |
| C:Biopolymer | 9,97837E7 | 1 | 9,97837E7 | 7,37 | 0,0147 |
| D:Fat method | 1,87662E7 | 2 | 9,3831E6 | 0,69 | 0,5137 |
| RESIDUAL | 2,30192E8 | 17 | 1,35407E7 | | |
| TOTAL (CORRECTED) | 1,57322E9 | 22 | | | |

All F-ratios are based on the residual mean square error.

**The StatAdvisor**
The ANOVA table decomposes the variability of COD into contributions due to various factors. Since Type III sums of squares (the default) have been chosen, the contribution of each factor is measured having removed the effects of all other factors. The P-values test the statistical significance of each of the factors. Since 3 P-values are less than 0,05, these factors have a statistically significant effect on COD at the 95,0% confidence level.

P-Value tells if the result depends on the factor studied. If P-Value of the Factor is 0, it means that it has 100% significance and that in this case the dependent variable, the COD result, will vary from the studied factor.

It will consider that the factor influences the dependent variable if the P-Value ranges from 0 to 0.05.

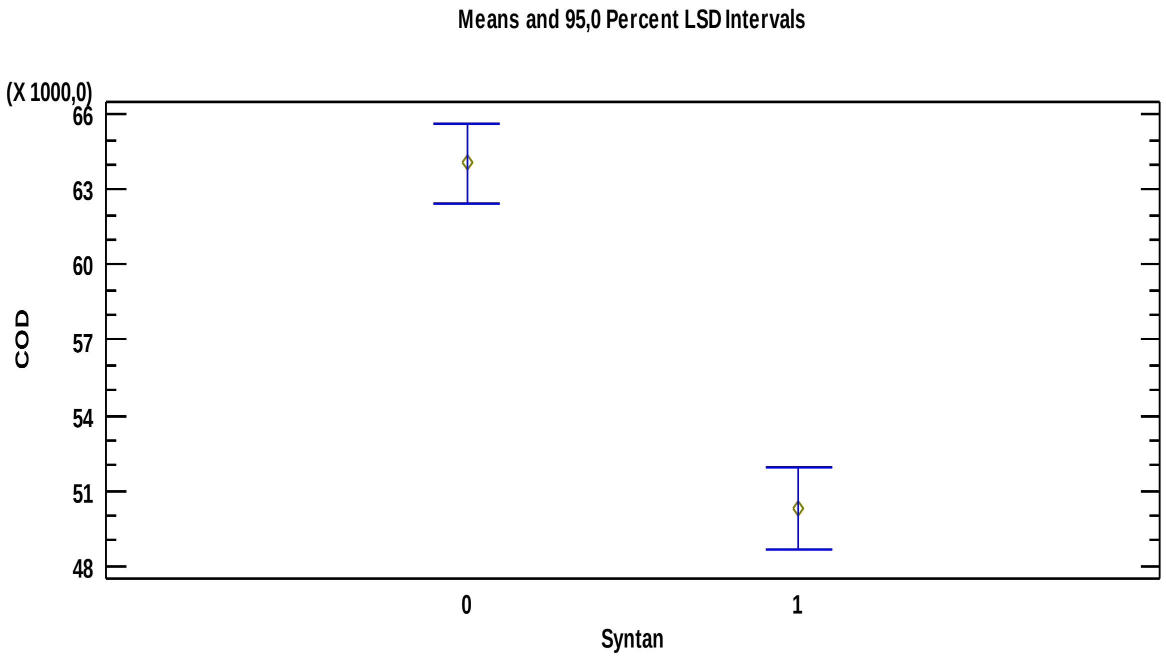
The ANOVA analysis was carried out taking into account the interactions between factors and the result has been that there were no significant interactions.

The final analysis was carried out considering that each factor is independent and that there wasn't interaction between factors that would influence the outcome.

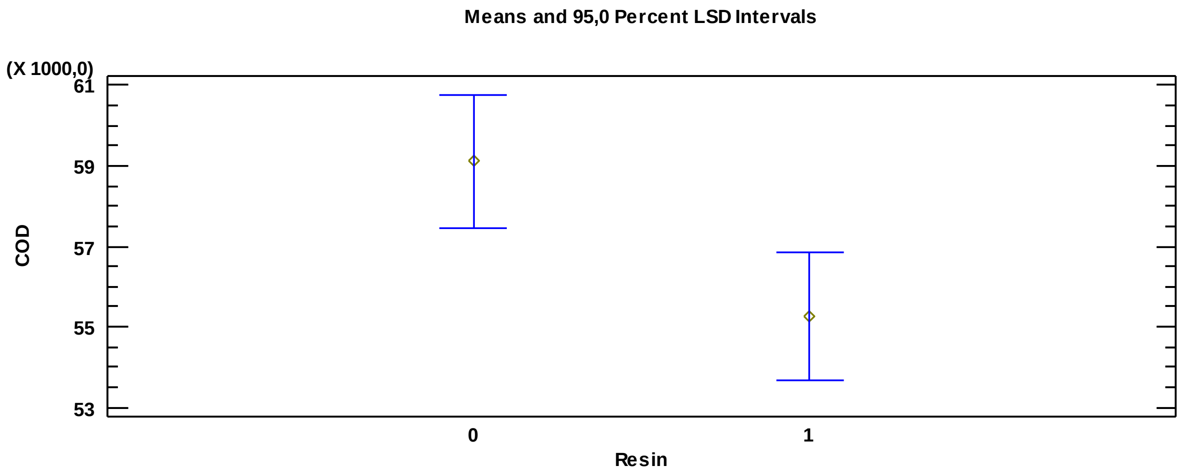
The P-value values indicate that 3 of the 4 factors studied do determine the COD result.

Below there are the graph of each factor.

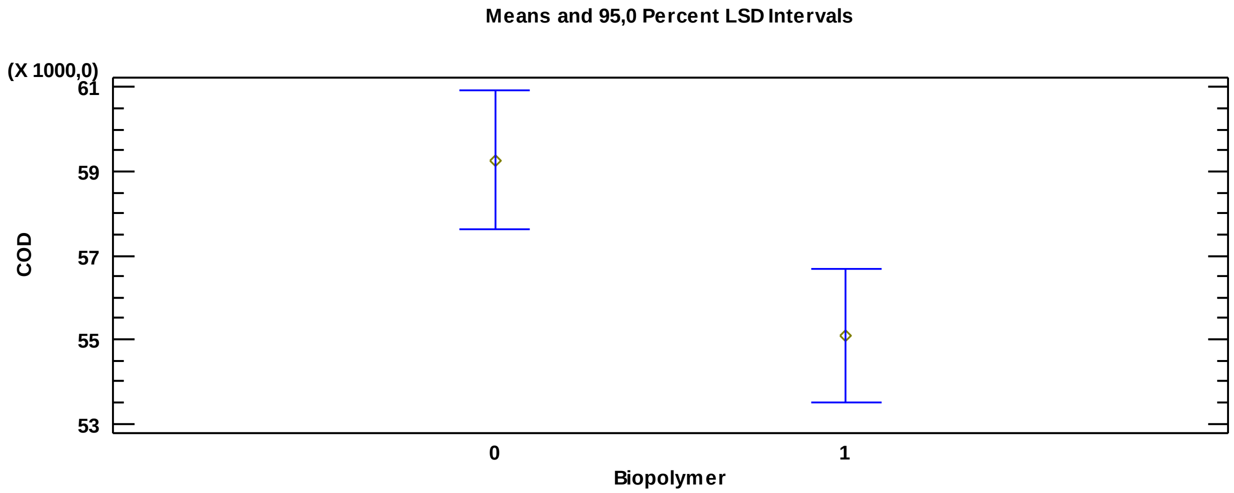
graphic 2, 3,4, 5: Fisher-Average graphics



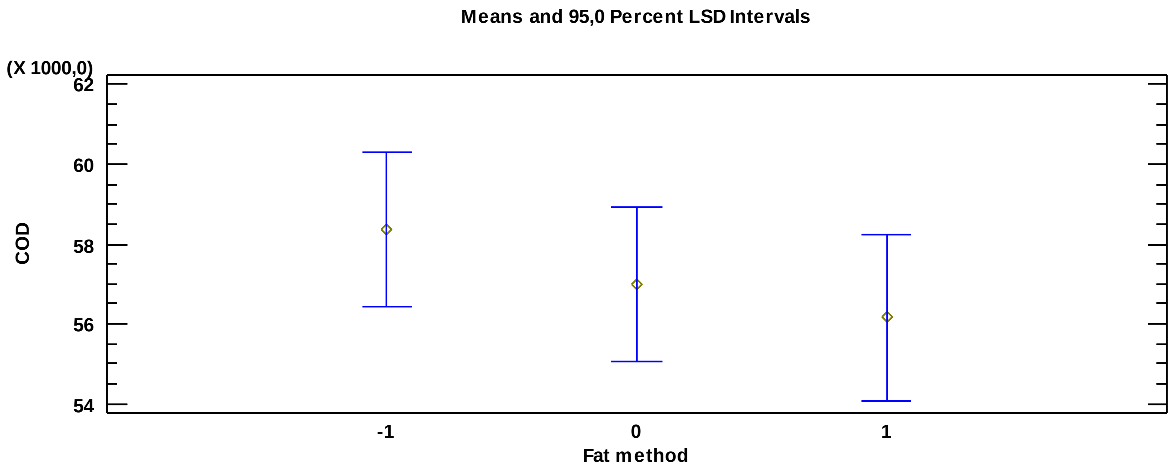

syntan or another, determines whether the COD value will be higher or lower. In this case, the syntan that provides better COD values is the value 1 that can be seen in the graph, which corresponds to the powder syntan 2 (phenolic). This indicates that with this substrate (wet-white) the phenolic components of syntan have a better affinity than the  liquid syntan diphenylsufone.




**Resin:** The P-value (0,0230) and the graphic indicate that on resin has better fixation. This is styrene melic 2 (ref. 1).




**Biopolymer:** The choice of the bipolymer also determines that the COD value is higher or lower. It can be seen in the graph and the P-value (0,0147). The best biopolymer to have lower COD values is the biopolymer powder 3 (ref. 1).




**Fatliquoring method:** The method of application of fatliquor isn't an influential factor in COD values. As seen in the graph, the COD values of the three application methods overlap each other. The P-Value (0,5137) has a value higher than 0.0500.

One possible explanation is that using whatever method, in the end the added load in the bath is the same.

### Organoleptic discussion of leather:

The subjective assessment of leather in this case as a general conclusion can be said that all samples could be a possible article. The differences between them are not many, as can be seen in the organoleptic assessment table.

The most important difference is when one syntan or the other is used. With liquid naphthalenesulfonic syntan, leathers like them more than with phenolic powder. Above all, differences can be seen in the level of fullness and softness of grain and flesh.

On the other hand, considering the resins, methacrylic acid has better results than styrene maleic, which is fine but has a bad combination with the synthetic phenolic. It behaves better with diphenylsulfone.

The difference between biopolymers is difficult to detect. The feeling is that the powder behaves better but the differences are minimal.

Taking into account the method of fatliquoring it can be seen that there is a certain improvement in the appearance of the leather when the fatliquoring is added 2/3 parts in the re-tanning and 1/3 part in the main fatliquoring. It seems that the fat enters better and the leather looks better when more amounts is added in the re-tanning. It could be tested in future studies of applying all the fat in re-tanning.

### *Conclusions:*

The multifactorial study and its assessment with the analysis of variance confirms that the COD of a process can be directly related to the use of a commercial product or other. In this case it has been confirmed that the main synthetic tanner of the process makes the COD value vary considerably. This syntan one that presents better results is the synthetic phenolic powder. It is also confirmed that with the choice of resin (styrene maleic)  and biopolymer (biopolymer powder 3), a lower COD of the process can be achieved.

As for the appearance of the leathers, they have very good characteristics and the differences are minimal. It should be noted that this has happened because before there have been 4 studies where they have been selecting the best products both in terms of exhaustion and appearance of leather.

Even so, it is concluded that it is better to apply the fatliquoring not all at the end, but in parts and even most during the re-tanning. The syntan that likes most is liquid diphenylsulfone, methacrylic acid as resin and biopolymer powder.

# 6. EXPERIMENTAL 6: *Final process and commercial leather articles.*

To finish the whole experimental part, it is decided to carry out two processes taking into account everything learned in the previous experiments and especially the results of ANOVA.

The same process structure is used but with some variants to improve the article.

It is decided to eliminate the neutralization process in a separate bath and it is carried out in the same tanning / re-tanning and fatliquoring bath. In this way it saves water both in the same neutralization process and in subsequent washing, and also time.

The fatliquor is added 2/3 parts in the re-tanning and 1/3 part in the main fatliquoring, but the lanolin / lecithin is added all at the end to look for a better surface touch/softness.

These processes will be with dye, so it can also appreciate the behavior of the dye with this process.

The products used are:

- Tare extract

- Powder syntan 2 (phenolic)

- Styrene maleic 2

- Biopolymer powder 3

- Sulphited oil 5

- Lanoline / Lecithin

## Process A:

The Spanish wet-white is used with which all tests have been performed. The dyeing is with a dark black.

Mechanization is like in the previous processes.

Leather goods article.

## Process B:

Another wet-white leather is used. This substrate has not been tested before with this process. It is a Scottish wet-white leather aimed at automotive upholstery articles.

The same process is performed as process A but the color is a reddish brown and the mechanization is different.

The mechanization is aimed at an upholstery article and the leather is sought to mark a bit of grain. The main difference with respect to the other mechanization is that it doesn't carry a vacuum and the leather is milled for 8 hours.

**Physical testing**

Once the two articles are dry and have rested, the following physical tests will be performed to determine if these commercial crusts exceed the quality specifications according to the item.

- IUP 6 (EN ISO 3376): Tensile strength and % elongation.
- IUP 8 (EN ISO 3377-2): Tear load.

| TARGET: | FINAL PROCESS A: Leather goods. | | | | Date: 6/5/2019 |
|---|---|---|---|---|---|
| Raw material: | Spanish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,5 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 50,0 | Water | 30º | | |
| | 2,0 | Neutralisation syntan *3 | | 45’ | pH: 4,5 – 5,0 |
| TAN / RETAN | 7,5 | Tara extract | | | |
| | 7,9 | Powder syntan 2 (phenolic) | | | |
| | 5,0 | Styrene maleic 2 | | 60’ | |
| | 50,0 | Water | 40º | | |
| | 2,8 | Sulphited Oil 5 | | 5’ | |
| | 1,0 | Black Dyestuff 1 | | | |
| | 1,5 | Black Dyestuff 2 (Acid black 210) | | | |
| | 7,5 | Tara extract | | | |
| | 7,9 | Powder syntan 2 (phenolic) | | | |
| | 5,0 | Styrene maleic 2 | | | |
| | 4,4 | Biopolymer powder 3 | | 90’ | |
| FATLIQUORING | 100,0 | Water | 45º | 5’ | |
| | 5,7 | Sulphited oil 5 | | | |
| | 3,5 | Lanoline and lecithin | | 90’ | |
| | 1,0 | Formic acid | | 15’ | |
| | 1,0 | Formic acid | | 20’ | |
| | 1,0 | Black Dyestuff 2 (Acid black 210) | | 15’ | |
| | 10,0 | Styrene maleic 2 | | 40’ | |
| | 0,5 | Formic acid | | 20’ | COD: 53.000ppm |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |

<u>Mechanical Operations:</u>

Horse up (overnight), setting-out, vacuum 2’/45ºC, hang dry, stake 6/7.

Process: 13: final process A for leather goods

Table 27: process summary A

## PROCESS SUMMARY A: LEATHER GOODS

| | |
|---|---|
| weight of hide (kg): | 2,9 |
| % water all process: | 800% |
| Total Volume water (L) | 23,2 |
| % water COD study: | 200% |
| Water COD study (L): | 5,8 |
| COD ppm: | 53000 |
| COD mg O2 / kg leather: | 106000 |
| Time (hours) | 7,5 |
| Tg (ºC) | 89 |
| Tear load (N/mm): | 84 |
| Tensile strenght (N/mm2) | 23 |
| % Elongation: | 53% |

| TARGET: | FINAL PROCESS B: Automotive | | | Date: | 6/5/2019 |
|---|---|---|---|---|---|
| Raw material: | Scotish W.W pretanned 1.3-1.5 mm | | % based on: | | Shaved weight |
| PROCESS | % | Products | T ºC | Run (min) | Remarks (pH, COD, ºBe, etc) |
| WET- BACK | 200,0 | Water | 30 º | | |
| | 0,5 | Surfactant (wetting) *1 | | | |
| | 0,5 | E.D.T.A *2 | | 30’ | |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| NEUTRALISE | 50,0 | Water | 30º | | |
| | 2,0 | Neutralisation syntan *3 | | 45’ | pH: 4,5 – 5,0 |
| TAN / RETAN | 7,5 | Tara extract | | | |
| | 7,9 | Powder syntan 2 (phenolic) | | | |
| | 5,0 | Styrene maleic 2 | | 60’ | |
| | 50,0 | Water | 40º | | |
| | 2,8 | Sulphited Oil 5 | | 5’ | |
| | 3,0 | Brown/red Dyestuff | | | |
| | 7,5 | Tara extract | | | |
| | 7,9 | Powder syntan 2 (phenolic) | | | |
| | 5,0 | Styrene maleic 2 | | | |
| | 4,4 | Biopolymer powder 3 | | 90’ | |
| FATLIQUORING | 100,0 | Water | 45º | 5’ | |
| | 5,7 | Sulphited oil 5 | | | |
| | 3,5 | Lanoline and lecithin | | 90’ | |
| | 1,0 | Formic acid | | 15’ | |
| | 1,0 | Formic acid | | 20’ | |
| | 0,5 | Brown/red Dyestuff | | 15’ | |
| | 10,0 | Styrene maleic 2 | | 40’ | |
| | 0,5 | Formic acid | | 20’ | COD: 47.000ppm |
| drain | | | | | |
| wash | 200,0 | Water | 25º | 5’ | |
| drain | | | | | |
| | | | | | |
| <u>Mechanical Operations:</u><br>Horse up (overnight), setting-out, hang dry toggling, stake 7/8, mill 8h. | | | | | |

Process: 14: final process B for automotive

Table 28: process summary B

## PROCESS SUMMARY B: LEATHER GOODS

| | |
|---|---|
| weight of hide (kg): | 2,2 |
| % water all process: | 800% |
| Total Volume water (L) | 17,6 |
| % water COD study: | 200% |
| Water COD study (L): | 4,4 |
| COD ppm: | 47000 |
| COD mg O2 / kg leather: | 94000 |
| Time (hours) | 7,5 |
| Tg ( ºC) | 91 |
| Tear load (N/mm): | 75 |
| Tensile strenght (N/mm2) | 19 |
| % Elongation: | 59% |

Quality guidelines and recommendations according to GERIC:

**Upholstery:**

Tear load: >50 N/mm

**Leather goods:**

Tensile strength (thickness < 2mm): 15N/mm$^2$

Tear load (thickness < 2mm): 50 N/mm

| | EVALUATION PARAMETERS | | | | | |
|---|---|---|---|---|---|---|
| EXPERIMENTAL / SAMPLE | Break | Fullness | Grain softness | Flesh softness | Colorful | AVERAGE |
| A) leather goods | 1,5 | 1,5 | 2 | 2 | - | 1,7 |
| B) automotive | 2 | 2 | 1 | 1 | - | 1,5 |

The two articles exceed the quality requirements according to the GERIC. The physical strengths of the two items would meet the specifications of most leather items. They are good results.

The organoleptic assessments are correct having the characteristics that the final article have.

# GENERAL CONCLUSIONS

This project has studied how the chemicals used in the tanning industry of a commercial chemical brand influence to the contamination of wastewater (at levels of Chemical Oxygen Demand) in a tanning / re-tanning / fatliquoring process for metal-free wet-white leathers.

It has also been studied how it affects the type of process and the addition of products in the appearance of leather and how to achieve a eco-friendly process that requires less water consumption and that the contamination of this is less.

It can be said that this study started from zero. First, the individual behavior of each product with the pre-tanned wet-white substrate was studied. It was concluded that some products had greater fixing power and the bath exhaustion was better (lower COD values). From the group of tanning products it highlight the synthetic powders, the resins have very good COD results and they are interesting products to use if you look for this type of ecological processes. The biopolymers are already oxidized organic matter but they give good results to the leather's appearance and fill a lot. The powder biopolymers have greater fixation. The fatliquors / oils are very independent each but that helped to be able to choose which of them have better bath exhaustion and have a better appearance on the leather.

Once the products were dealing with were known, a real wet-end process was applied by applying and combining these products. The results said that once these products were applied in the process, the COD differences they had individually are not appreciated as much. It also worked on how to apply the fatliquors and if it was possible to apply all the products in the same bath and also obtain a good article since the amount of water consumed and the total COD load was considerably reduced.

These processes were then compared but using a wet-blue substrate instead of wet-white and it was possible to verify that the COD values were very similar and even better using the Wet-white. It is concluded that in processes like this, using wet-white instead of wet-blue doesn’t mean that the anionic charge has less fixation on substrate.

A study was also carried out to see if using the resins, since they are the products that least raise the COD value, applied at the end of the process in the acidic fixing medium, could even help fix the products and decrease the final value of COD. The results obtained indicated that they didn’t increase the COD value and that they gave the final article better characteristics, and even on some occasion they decreased the final COD value of the bath.

With all these previous tests the multifactorial experimental process has already been designed taking into account all the information obtained and the previous knowledge of the products. The objective was to see if the COD value was directly dependent on the products added in the recipe. It is concluded that in the case of the choice of the main syntan (powder syntan 2 – phenolic), the resin (styrene maleic) and the biopolymer (biopolymer powder 3), choosing one or the other, are totally influential factors in terms of the final COD value.

Finally the process is adjusted again and two final articles with very good characteristics and appearance are made.

It can be said that by studying well the chemical products of the industry that are going to be used, their affinity with the wet-white raw material, designing and adjusting a process that has good organoleptic results and that it don’t have a great water consumption. It is possible to obtain metal-free articles with very good characteristics and with ecological processes with low water consumption and with a polluting load of the bath (COD) not higher than a wet-blue leather process.

As a final comment, the study is summarized, with the design of a tanning / re-tanning process that allows to obtain metal-free articles minimizing the COD values by choosing re-tanning products. This process allows manufacturing leathers that exceeds the quality specifications of the physical and organoleptic properties required by international organizations.

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# ANNEXES

## Annex 1: Chemical products used of TRUMPLER.

### Tare extract (TRUPOTAN TR)

Trumpler
simply good chemistry

**TRUPOTAN® TR**
vegetable tanning agent

| | |
|---|---|
| Basis: | pyrogallol tannins, tara |
| Appearance: | light brown powder |
| pH value (1 : 10): | approx. 3.5 |
| Light fastness: | good |
| Heat yellowing: | medium |

Properties:

TRUPOTAN TR is a vegetable tanning agent produced from Tara pods.

TRUPOTAN TR is applied in the tanning and retanning of chrome-free leathers and also in the retannage of wet blue.

TRUPOTAN TR brings an increase in fullness and improvement in the grain tightness. Crust leathers produced with TRUPOTAN TR have a very light colour, but when dyed very level, clean and brilliant dye shades.
All leathers produced with TRUPOTAN TR have a good softness with a full round handle.

**Application:**

For the retannage of chrome-free car upholstery leather the following application quantities are recommended:

8 - 12 % TRUPOTAN TR
+ 7 - 10 % TRUPOTAN GD

In the retannage of wet blue a portion of TRUPOTAN TR will improve the fullness and grain tightness.

For the retannage of most leathers an addition of 2 % TRUPOTAN TR will assist to suppress the formation of hexovalent chromium.

## Powder syntan 1 (TRUPOTAN GSX)

Trumpler
simply good chemistry

# TRUPOTAN® GSX

| | |
|---|---|
| Basis: | Synthetic retanning agent. |
| Uses: | Compact retannings with light stand. |
| Appearance: | Beige powder. |
| Charge: | Anionic. |
| Active matter: | Approx. 94%. |
| 10% pH Dissolution: | Approx. 2,0. |

**TRUPOTAN GSX** has been developed for tanning all kinds of leathers and skins whenever stand or spring is required

**TRUPOTAN GSX** is not easily soluble in water but can be added in powder to the drum. **TRUPOTAN GSX** fills and compacts the leather during the tanning process, giving fullness and mellowness to the grain.

**TRUPOTAN GSX** can be combined to resin or vegetal retanning agents.

Leathers retanned with **TRUPOTAN GSX** show a light stand.

**Uses**

**TRUPOTAN GSX** is specially suited for the retanning of sheep or goatskins for shoe and lining.

To retan heavy, chrome retanned leathers, we suggest using **TRUPOTAN GSX** together with resin or vegetal tanning agents.

## Powder syntan 2 (TRUPOTAN BLP)

Trumpler
Creamos buena química

# TRUPOTAN® BLP

| | |
|---|---|
| Base: | Agent de retannage synthétique à base phénolique. |
| Application: | Cuirs de tannage végétal, vêtements, nappas, nubuck, velours. |
| Aspect: | Poudre de couleur beige clair. |
| Charge: | Anionique. |
| Matieres actives: | Environ 95 %. |
| pH dissolution 10%: | Environ 4.0. |

Le **TRUPOTAN BLP** est un tannin de remplacement utilisé pour le retannage du cuir au chrome donnant des cuirs pleins avec un bon toucher.

Le **TRUPOTAN BLP** étant peu astringeant, il modifie très peu le grain.

Le **TRUPOTAN BLP** est approprié pour la fabrication des cuirs très divers, doublure, empeigne et cuirs pour vêtements.

Le **TRUPOTAN BLP** se distingue par sa solidité à la lumière. C'est grâce à ses propriétés que le **TRUPOTAN BLP** est choisi pour la fabrication de cuirs blancs.

Le **TRUPOTAN BLP** possède un important effet dispersant sur la partie moins soluble des agents de retannage végétaux et peut être utilisé avec des extraits naturels pour le tannage et retannage végétal. Le cuir présente alors une couleur plus claire.

Son grand pouvoir de tannage le rend idéal pour être employé comme agent de tannage unique pour le tannage des cuirs entièrement blancs ou pour le tannage des cuirs de reptiles.

## Powder syntan 4 (TRUPOTAN SW)

Trumpler
simply good chemistry

# TRUPOTAN® SW

replacement syntan

| | |
|---|---|
| Basis: | diphenyl condensation product |
| Appearance: | white powder |
| Charge: | anionic |
| Active matter: | approx. 96 % |
| pH value (1 : 10): | approx. 4.5 (+ 0.5) |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN SW** is a replacement syntan for the retannage of all types of leather.

**TRUPOTAN SW** has an excellent optical brightening effect and is therefore ideal for production of white and pastel coloured leather.

**TRUPOTAN SW** gives leather an outstanding softness with excellent fullness and round handle.

**TRUPOTAN SW** is ideal for the production of leathers that require low free formaldehyde values.

**Application:**

In the retannage of wet blue a quantity of between 4 and 8 % **TRUPOTAN SW,** calculated on the wet blue weight, is recommended.

For the retannage of chrome-free car upholstery leather, up to 10 % of **TRUPOTAN SW** is recommended to support the vegetable tannage.

For the retannage of sheep wet blue for softy clothing leather or milled leather a quantity from 4 to 8 % **TRUPOTAN SW** is normally recommended.

## Liquid syntan 1 (TRUPOTAN CFP)

Trumpler
Creamos buena química

# TRUPOTAN® CFP

| | |
|---|---|
| Composition chimique: | Produit de tannage synthétique préparé à base de polymère modifié et diphénilsulphone. |
| Aspect: | Liquide ambre. |
| Matière active: | approx. 38 %. |
| pH (1:10): | approx. 4. |

**TRUPOTAN CFP** est un produit synthétique conçu pour utiliser sur tous types de peaux et cuirs, pendant les étapes de tannage et retannage.

**TRUPOTAN CFP** donne des cuirs très blancs et par conséquent, il est idéal pour la production de cuirs blancs et pastels.

**TRUPOTAN CFP** donne des peaux très souples, pleines ayant un excellent toucher.

**TRUPOTAN CFP** possède des propriétés solides à la lumière et au vieillissement.

**TRUPOTAN CFP** peut être utilisé pour le pre-tannage d'articles libres de chrome sur tous types de peaux. Utilisé seulement sur des peaux de mouton, on peut obtenir des valeurs de TG d'approximativement 80ºC.

**TRUPOTAN CFP** utilisé comme produit de retannage confère des peaux foulonnées très souples avec un grain fin et régulier.

**Applications**

Comme produit de retannage sur peaux de bovins wet-blue ou wet-white: 5% - 15% sur poids dérayé.

Pour le retannage de peaux de mouton : 6 - 10% sur poids dérayé.

Comme agent unique sur le pre-tannage ou combiné avec d'autres agents: 10% - 20% sur poids dérayé.

Pour le retannage de peaux pour tapisserie sans chrome: 10% - 20% sur le poids dérayé combiné avec d'autres agents de tannage à base végétale ou synthétique.

## Liquid syntan 2 (TRUPOTAN WSN)

Trumpler
simply good chemistry

# TRUPOTAN® WSN
replacement syntan

| | |
|---|---|
| Basis: | diphenyl condensation product |
| Appearance: | yellow liquid |
| Charge: | anionic |
| Active matter: | approx. 38 % |
| pH value (1 : 10): | approx. 4 |
| Light fastness: | good |
| Heat yellowing: | good |

Properties:

TRUPOTAN WSN is a replacement syntan for the retannage of all types of leather.

TRUPOTAN WSN has an excellent optical brightening effect and is therefore ideal for production of white and pastel coloured leather.

TRUPOTAN WSN gives leather an outstanding softness with excellent fullness and round handle.

TRUPOTAN WSN is ideal for the production of leathers that require low free formaldehyde values.

Application:

In the retannage of wet blue a quantity of between 8 and 15 % TRUPOTAN WSN, calculated on the wet blue weight, is recommended.

For the retannage of chrome-free car upholstery leather, up to 20 % of TRUPOTAN WSN is recommended to support the vegetable tannage.

For the retannage of sheep wet blue for softy clothing leather or milled leather a quantity from 6 to 10 % TRUPOTAN WSN is normally recommended.

## Acrylic 1 (TRUPOTAN RXL)

Trumpler
simply good chemistry

# TRUPOTAN® RXL

polymer retanning agent

| | |
|---|---|
| Basis: | acrylic polymer |
| Appearance: | pale coloured viscous liquid |
| Charge: | anionic |
| Active matter: | approx. 30 % |
| pH value(1 : 10): | approx. 5 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN RXL** is a high molecular weight polymer retanning agent intended for use on a wide range of leathers e.g. shoe upper, upholstery and garment leathers.

**TRUPOTAN RXL** is fully water soluble and due to its specifically designed make up can be used across a wide pH-range.

**TRUPOTAN RXL** possesses outstanding resistance to light and heat yellowing and is therefore ideally suited to the production of white and pastel shade leathers.

**TRUPOTAN RXL** exhibits low foaming characteristics and due to its well balanced reactivity and pH will exhaust readily from retanning baths.

Leathers treated with **TRUPOTAN RXL** exhibit outstanding fullness and tightness whilst retaining fine smooth grain characteristics and an extremely soft pleasant handle.

## Acrylic 2 (TRUPOTAN R83)

Trumpler
simply good chemistry

# TRUPOTAN® R83
polymer retanning agent

| | |
|---|---|
| Basis: | polyacrylic acids |
| Appearance: | viscous liquid |
| Charge: | anionic |
| Active matter: | approx. 33 % |
| pH value(1 : 10): | approx. 3.5 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN R83** is a retanning agent based on acrylic acids for the retanning of all types of leathers.

**TRUPOTAN R83** produces leathers with excellent fullness and softness together with a tight, fine grain.

**TRUPOTAN R83** improves the buffing properties.

**TRUPOTAN R83** has bleaching properties and is very suitable for the production of white and pastel dyed leathers.

**Application:**

In the retanning between 2 and 4 % **TRUPOTAN R83** is recommended, calculated on shaved weight. Optimal fullness and effect with **TRUPOTAN R83** is achieved when added after running with neutralisation syntans.

Increasing the float temperature or the addition of formic acid increases the uptake and exhaustion of **TRUPOTAN R83**.

## Acrylic 3 (TRUPOTAN RS)

Trumpler
simply good chemistry

# TRUPOTAN® RS

polymer tanning agent

| | |
|---|---|
| Basis: | modified metacrylic polymer |
| Appearance: | colourless viscous liquid |
| Charge: | anionic |
| Active matter: | approx. 30 % |
| pH value(1 : 10): | approx. 3 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN RS** is a polymer tanning agent for application in the tannage or retannage processes where improved fullness and grain quality are required.

**TRUPOTAN RS** produces fine and tight grained leathers without reducing softness and is therefore suitable for application in all types of leather production e.g. white shoe upper leather, car upholstery and garment nappa leathers.

**TRUPOTAN RS** is fully water soluble and stable to chrome and aluminium salts and may be utilised across a wide pH range.

**TRUPOTAN RS** can improve the buffing properties of nubuck leather production.

**Application:**

During chrome tannage the **TRUPOTAN RS** is best added 90 mins. after the chromium.
In rechroming processes the **TRUPOTAN RS** is best applied 40 mins. after the chrome addition.

**TRUPOTAN RS** may be applied together with other anionic retanning materials, or after fatliquoring and before acid fixation.

In every application **TRUPOTAN RS** should be diluted (1:5 with water).

## Acrylic 4 (TRUPOTAN NCR)

Trumpler
simply good chemistry

# TRUPOTAN® NCR
polymer retanning agent

| | |
|---|---|
| Basis: | modified acrylic polymer |
| Appearance: | viscous liquid |
| Charge: | anionic |
| Active matter: | approx. 30 % |
| pH value(1 : 10): | approx. 4 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN NCR** is a polymer retanning agent, based on modified acrylic polymers intended for the tanning and retanning of all types of leather.

**TRUPOTAN NCR** improves the fullness and grain tightness producing especially fine grained leather.

**TRUPOTAN NCR** encourages a good chrome fixation and distribution in the final leather.

**TRUPOTAN NCR** improves the penetration of the dyestuff with minimal loss of dye intensity.

**Application:**

In chrome tanning between 0.5 and 1.0 % **TRUPOTAN NCR** can be applied to improve the grain tightness of the wet blue. The pH-value of the chrome tanning should lie over pH 3 before application of the **TRUPOTAN NCR**.

In the rechrome between 1.5 to 3.0 % **TRUPOTAN NCR** may be applied, based on shaved weight, to improve the fullness and grain tightness.

## Acrylic 5 (TRUPOTAN RKM)

Trumpler
simply good chemistry

# TRUPOTAN® RKM

polymer retanning agent

| | |
|---|---|
| Basis: | polyacrylic acid compound |
| Appearance: | viscous liquid |
| Charge: | anionic |
| Active matter: | approx. 30 % |
| pH value(1 : 10): | approx. 7.5 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN RKM** is a polymer retanning agent on the basis of polyacrylic acids intended for the retannage of all types of leather.

**TRUPOTAN RKM** increases the fullness and grain tightness.

**TRUPOTAN RKM** eases the penetration of dyestuffs without reducing the dye intensity.

**Application:**

**TRUPOTAN RKM** can be applied in the neutralisation process or in the retannage.
After neutralisation between 2 and 4 % **TRUPOTAN RKM**, based on shaved weight, can be used to increase the softness and fullness of the leather.

In the retannage between 2 and 6 % **TRUPOTAN RKM** can be applied, based on the shaved weight, to improve the grain tightness.

## Styrene-maleic 1 (TRUPOTAN NEC)

Trumpler
simply good chemistry

# TRUPOTAN® NEC

| | |
|---|---|
| Basis: | Polymer: Styrene-maleic. |
| Application: | Retanning of all kinds of leather. |
| Appearance: | Slightly yellowish liquid. |
| Charge: | Anionic. |
| Active matter: | Approx. 25%. |
| 10% pH Dissolution: | Approx. 5,5. |
| Acid stability: | Good. |
| Hard water stability: | Excellent. |
| Vegetal stability: | Excellent. |
| Light fastness: | Excellent. |
| Ageing fastness: | Excellent. |

**Properties and application**

**TRUPOTAN NEC** is completely water soluble and compatible with most TRUPOTAN retanning agents.

- The most usual vegetal retanning agents.
- Most of anionic synthetic retanning agents.
- Most of acrylic retanning agents.

Leathers processed with **TRUPOTAN NEC** exhibit outstanding fullness together with good grain tightness.

**TRUPOTAN NEC** used in the same retanning bath gives more mellow handles than when applied as a usual retanning agent. Nevertheless, both cases show extremely smooth grain and good tightness.

Further dyeings with anionic dyestuffs are always clean and even.

## Filler (TRUPOTAN TFP)

Trumpler
simply good chemistry

# TRUPOTAN® TFP

filling agent

| | |
|---|---|
| Basis: | filling agent based on organic and inorganic components |
| Appearance: | white powder |
| Active matter: | approx. 95 % |
| pH value (1 : 10): | approx. 7 |
| Light fastness: | good |
| Heat yellowing: | good |

**Properties:**

**TRUPOTAN TFP** is a filling agent specifically designed to fill loose structured areas of the skin or hide.

**TRUPOTAN TFP** when used in the production of splits or nubuck leathers either by direct or crusting methods will greatly assist the buffing capacity and help reduce irregularities in the leather.

**TRUPOTAN TFP** disperses readily in water and exhibits excellent penetration and exhaustion properties when utilised correctly.

Poor quality hides which exhibit loose belly areas and a marked tendancy to veininess can be clearly upgraded by the use of **TRUPOTAN TFP** thus allowing improved selection and better profitability to be achieved.

**TRUPOTAN TFP** will not adversely affect the intensity or brightness of dyeings produced with anionic dyestuffs.

The use of **TRUPOTAN TFP** in the production of water resistant leather will not negatively influence the hydrophobic characteristics.

## Styrene-maleic (TRUPOTAN WRT)

Trumpler
simply good chemistry

# TRUPOTAN® WRT

auxiliary syntan

| | |
|---|---|
| Basis: | styrene malein copolymer |
| Appearance: | viscous liquid |
| Charge: | anionic |
| Active matter: | approx. 34 % |
| pH value (1 : 10): | approx. 8.5 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

Properties:

TRUPOTAN WRT is a styrene malein copolymer retanning agent.

TRUPOTAN WRT is suitable for the production of waterproof shoe upper leather.

TRUPOTAN WRT improves greatly the grain tightness.

With TRUPOTAN WRT a leather with good stand, a fine elastic grain and a pleasant handle is produced.

TRUPOTAN WRT supports extraordinarily the properties of the waterproof fatliquors and is very suitable to be used together with a TRUPOSIST® -system.

Application:

In the retanning normally between 3 and 6 % TRUPOTAN WRT, calculated on shaved weight, is utilised. The quantity applied depends on the type of leather and required fullness.

## Biopolymer powder 1 (TRUPOTAN UTH)

Trumpler
simply good chemistry

# TRUPOTAN® UTH

natural-based polymer

| | |
|---|---|
| Basis: | modified natural amphoteric polymer |
| Appearance: | beige powder |
| Charge: | weakly anionic |
| Active matter: | approx. 90 % |
| pH value(1 : 10): | approx. 8 |
| Light fastness: | good |
| Heat yellowing: | good |

**Properties:**

**TRUPOTAN UTH** is a natural based polymer tanning agent with amphoteric character, it is suitable for the retannage of all types of leathers.

**TRUPOTAN UTH** improves the fullness and the grain tightness, especially in the more looser structured areas of the hide.

**TRUPOTAN UTH** improves greatly the buffing properties and supports more intensive and brilliant dyeings with anionic dyestuffs.

**TRUPOTAN UTH** does not affect waterproofing properties.

**Application:**

**TRUPOTAN UTH** applied in the neutralization bath will supply full and softer leathers.

**TRUPOTAN UTH** applied in retanning bath will supply full but firmer leathers.

**TRUPOTAN UTH** can be applied with dosis from 3 to 8 % (on shaved weight), depending on desired effect and raw material used.

**TRUPOTAN UTH** is also suitable for the retanning of chrome free leather.

## Biopolymer powder 2 (TRUPOTAN UPH)

Trumpler
simply good chemistry

# TRUPOTAN® UPH

natural-based polymer

| | |
|---|---|
| Basis: | modified protein |
| Appearance: | light brown powder |
| Charge: | anionic |
| Active matter: | approx. 90 % |
| pH value(1 : 10): | approx. 8 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN UPH** is a natural based polymer tanning agent.

**TRUPOTAN UPH** is suitable for the retannage of all types of leathers.

**TRUPOTAN UPH** improves the fullness and the grain tightness, especially in the more looser structured areas of the hide.

**TRUPOTAN UPH** improves greatly the buffing properties.

**Application:**

**TRUPOTAN UPH** can be applied in all process steps, for example in the neutralisation, in the retannage as well as in the fatliquoring process before fixing with formic acid.

The applied quantity of **TRUPOTAN UPH** normally lies between 2 and 4 %, calculated on the shaved weight.

**TRUPOTAN UPH** is also very good for the retanning of chrome-free car upholstery leather.

### Biopolymer powder 3 (TRUPOTAN BIO 08P)

Trumpler
Creamos buena química

# TRUPOTAN® BIO-08P

| | |
|---|---|
| Basis: | Low molecular weight modified biopolymer. |
| Use: | Retanning of any kind of leather, organic or mineral tanned. Formaldehide free alternative to melamine or diciandiamide resins. |
| Appearance: | Powder. |
| Charge: | Anphoteric. |
| pH | Approx. 8. |
| Light fastness: | Good. |
| Ageing fastness: | Good. |

**Properties**

**TRUPOTAN BIO-08P** is an innovative chemical obtained by modification of natural occuring polymers. It’s molecular weight has been adjusted in a narrow range.

Used as retanning agent, **TRUPOTAN BIO-08P** imparts to the leather fullnes, good filling and mellow handle.

Leathers produced with TRUPOTAN BIO-08 will show firm grain, standing out always by its level, fine and silky touch.

When used in the retanning proces or in the dyeing bath, **TRUPOTAN BIO-08P** produces more firm leathers with a marked filling efect.

Both on chrome and chrome free leather, the use of **TRUPOTAN BIO-08P** improves the dyeing operation with anionic dyestuffs. Levellness, brilliance and intensity are normally improved.

**TRUPOTAN BIO-08P** as a retanning agent in the production of splits and suede articles, improves the buffing capacity of the leather and provides really short an regular nap.

When producing direct nubuc, using **TRUPOTAN BIO-08P** in the retanning bath will provide both improvement of dye intensity together with excellent buffing capacity.

## Biopolymer powder 4 (TRUPOTAN BIO BOX)

Trumpler
simply good chemistry

# TRUPOTAN® BIO-BOX

modified biopolymer

| | |
|---|---|
| Basis: | modified biopolymer with low molecular weight |
| Appearance: | light brown powder |
| Charge: | amphoteric |
| pH value(1 : 10): | approx. 7 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

### Properties:

**TRUPOTAN BIO-BOX** is a natural-based biopolymer suitable for the production of all types of leather.

**TRUPOTAN BIO-BOX** is free of formaldehyde.

**TRUPOTAN BIO-BOX** imparts to the leather a good fullness and a mellow handle.

**TRUPOTAN BIO-BOX** produces leather with a firm grain and a silky touch.

**TRUPOTAN BIO-BOX** improves the dye intensity and levelness on chrome free leathers as well as on chrome leathers.

For the production of splits or other suede articles **TRUPOTAN BIO-BOX** produces a short and even nap with a very good writing effect.

**TRUPOTAN BIO-BOX** has no negative influence on waterproofing articles.

### Application:

The **TRUPOTAN BIO-BOX** can be applied in the retanning process as well as in the dyeing process before fixing with formic acid.

The applied quantity normally lies between 4 - 6 %, based on shaved weight.

## Biopolymer liquid 1 (TRUPOTAN BIO 02L)

Trumpler
Creamos buena química

# TRUPOTAN® BIO 02L

| | |
|---|---|
| Basis: | High molecular weight modified biopolymer. |
| Use: | Upholstery, automotive, furniture, footwear and leather goods. |
| Appearane: | Amber liquid. |
| Charge: | Amphoteric. |
| pH value (1 : 10): | Approx. 7 |
| Light fastness: | Excellent. |
| Ageing fastness: | Excellent. |

Properties

**TRUPOTAN BIO 02L** is an innovative chemical obtained by modification of natural occurring polymers. Its molecular weight has been adjusted in a narrow range.

**TRUPOTAN BIO 02L** is especially recommended for the retannage of upholstery, car upholstery and softy footwear and leather goods. Leathers obtained will show full, round and light handles.

**TRUPOTAN BIO 02L** used in the retanning & fatliquoring stage will improve penetration and distribution of chemicals, getting as a result deeper softnes and better levelling in the final article. Thanks to its amphoteric character, leathers retanned with **TRUPOTAN BIO 02L** will always exhibit an excellent dyeing behaviour. Dyeings will aways show good levelling and brillance.

**TRUPOTAN BIO 02L** can be used in the production of waterproofing articles without loss of properties.

## Application

Depending on the leather and on the required article, next dosage could be used:

In neutralisation stage: 4% - 6% - In retanning stage: 4% - 8%

### Biopolymer liquid 2 (TRUPOTAN BIO 03L)

Trumpler
simply good chemistry

# TRUPOTAN® BIO-03L

## modified biopolymer

| | |
|---|---|
| Basis: | modified biopolymer with low molecular weight |
| Appearance: | yellowish liquid |
| Charge: | anionic |
| pH value(1 : 10): | approx. 6 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN BIO-03L** is a natural-based biopolymer suitable for the production of any types of leather from small skins e.g. goat and sheep.

**TRUPOTAN BIO-03L** is free of formaldehyde.

**TRUPOTAN BIO-03L** imparts to the leather a good fullness combined with a round and light handle.

**TRUPOTAN BIO-03L** has a high dispersing effect which results in brilliant and even dyeing.

**TRUPOTAN BIO-03L** has no negative influence on waterproofing articles.

**Application:**

**TRUPOTAN BIO-03L** can be applied undiluted in the neutralisation process and/or retanning process.

The applied quantity normally lies between 8 – 12 %, based on shaved weight.

## Biopolymer liquid 3 (TRUPOTAN BIO 05L)

Trumpler
simply good chemistry

# TRUPOTAN® BIO-05L

modified biopolymer

| | |
|---|---|
| Basis: | modified biopolymer with high molecular weight |
| Appearance: | viscous amber liquid |
| Charge: | amphoteric |
| pH value(1 : 10): | approx. 4 |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOTAN BIO-05L** is a natural-based biopolymer suitable for the production of a wide range of articles, but especially for split, suede and nubuck leathers.

**TRUPOTAN BIO-05L** is free of formaldehyde, phenols and chrome.

**TRUPOTAN BIO-05L** allows, due to its amphoteric character, to produce really different effects on leather simply by adjusting application parameters (pH, temperature, ionic charge).

**TRUPOTAN BIO-05L** produces leather with exceptional buffing properties and provides a short, compact and more evenly nap.

**TRUPOTAN BIO-05L** improves the dye-ability.

**TRUPOTAN BIO-05L** has no negative influence on waterproofing articles.

**TRUPOTAN BIO-05L** is compatible with most retanning agents and fatliquors used in the leather processing. But it is always recommendable to check stability when using **TRUPOTAN BIO-05L** together with vegetable extracts in the same bath and especially at low pH values.

## Sulphited oil 1 (TRUPON AMF)

Trumpler
simply good chemistry

# TRUPOSOL® AMF

fatliquor for softy leathers

| | |
|---|---|
| Basis: | sulphited readily renewable raw materials |
| Appearance: | beige, pasty |
| Charge: | anionic |
| Active matter: | approx. 43 % |
| pH value(1 : 10): | approx. 7.5 |
| Acid stability: | good |
| Salt stability: | good |
| Light fastness: | good |
| Heat yellowing: | good |

**Properties:**

**TRUPOSOL AMF** is a fatliquor designed to produce outstanding softness on all types of leather.

**TRUPOSOL AMF** meets the stringent demands laid down for automobile upholstery leathers.

Leathers fatliquored with **TRUPOSOL AMF** exhibit outstanding inner softness coupled with extremely fine grain characteristics and a pleasant round handle. **TRUPOSOL AMF** will enhance the colour value of dyed leather.

**Application:**

**TRUPOSOL AMF** can be used alone or in combination with other anionic fatliquors.

**TRUPOSOL AMF** should be prepared for use by adding it to a minimum of five times its own volume of water at 50 °C whilst stirring.

Quantities to be used will depend upon the processing stage and the degree of softness required, but will normally vary between 8 - 14 %, based on shaved weight.

### Sulphited oil 2 (TRUPOSOL GF)

Trumpler
simply good chemistry

# TRUPOSOL® GF

universal fatliquor, especially for softy leathers

| | |
|---|---|
| Basis: | oxidised and sulphited natural fatty substances |
| Appearance: | brown viscous oil |
| Charge: | anionic |
| Active matter: | approx. 70 % |
| pH value (1 : 10): | approx. 7 |
| Acid stability: | excellent |
| Salt stability: | excellent |
| Chrome stability: | excellent |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOSOL GF** is a highly sulphited fatliquor based on high quality natural fatty substances. Due to its outstanding stability to electrolytes, **TRUPOSOL GF** can be used in chrome and FOC tannages and retannages, to promote a very good and even inner softness, tight and flat grain characteristics, along with excellent fullness, and pleasant warm handle.

Excellent lightfastness and heat yellowing stabilities make **TRUPOSOL GF** a highly versatile product, suitable to automotive and upholstery leather applications in addition to shoe upper and garment leathers.

## Sulphited oil 3 (TRUPOSOL SAM)

Trumpler
simply good chemistry

# TRUPOSOL® SAM

fatliquor for automobile and upholstery leather

| | |
|---|---|
| Basis: | sulphited natural and synthetic fatting substances |
| Appearance: | brown oil |
| Charge: | anionic |
| Active matter: | approx. 65 % |
| pH value(1 : 10): | approx. 7 |
| Acid stability: | medium |
| Salt stability: | good |
| Chrome stability: | medium |
| Light fastness: | excellent |
| Heat yellowing: | good |

**Properties:**

**TRUPOSOL SAM** is a semi synthetic sulphited fatliquor which can be used to good effect on all types of softy leathers including upholstery and automotive upholstery.

**TRUPOSOL SAM** exhibits outstanding softness and fullness coupled with well lubricated grain characteristics and a pleasant round handle.

Leathers fatliquored with **TRUPOSOL SAM** possess extremely good fogging characteristics in both reflectometric and gravimetric test procedures.

**TRUPOSOL SAM** is fish oil free and based upon environmentally friendly, readily renewable raw materials.

**TRUPOSOL SAM** exhausts readily from the fatliquoring bath thus producing extremely low COD levels in waste water.

## Sulphited oil 4 (TRUPON FL1)

Trumpler
simply good chemistry

# TRUPONOL® FL1

fatliquor for vegetable tanned and retanned leather

| | |
|---|---|
| Basis: | sulphited oxidised fish oil |
| Appearance: | red brown oil |
| Charge: | anionic |
| Active matter: | approx. 90 % |
| pH value(1 : 10): | approx. 6.5 |
| Acid stability: | good |
| Salt stability: | good |
| Chrome stability: | good |
| Light fastness: | good |
| Heat yellowing: | medium |

**Properties:**

**TRUPONOL FL1** is a highly sulphited fatliquor based on specially selected fish oil.

**TRUPONOL FL1** exhibits outstanding softening properties coupled with a fine mellow handle.

In addition to its use in softy and upholstery leathers **TRUPONOL FL1** can be used to advantage in the production of vegetable tanned and retanned leathers where it will help to maintain good grain lubrication characteristics.

**Application:**

**TRUPONOL FL1** can be utilised to good effect at levels of between 1 - 3 %, based upon shaved weight, in rechroming and neutralisation.

In the main fatliquoring process **TRUPONOL FL1** can be used at levels of 2 % together with other **TRUPON**® fatliquors.

## Sulphited oil 5 (TRUPON OSL)

Trumpler
simply good chemistry

# TRUPON® OSL

fatliquor for garment and nappa leather

| | |
|---|---|
| Basis: | sulphited and phosphatised triglycerides and nonionic stabilisers |
| Appearance: | red brown, semi viscous oil |
| Charge: | anionic / nonionic |
| Active matter: | approx. 93 % |
| pH value (1 : 10): | approx. 7 |
| Acid stability: | excellent |
| Salt stability: | excellent |
| Chrome stability: | excellent |
| Light fastness: | excellent |
| Heat yellowing: | medium |

Properties:

TRUPON OSL is a highly effective fatliquor for the production of light, fluffy clothing and softy leathers.

TRUPON OSL can be used to good effect in the fatliquoring of bovine and ovine clothing leathers, where it will confer outstanding softness and handle coupled with the ability to produce an extremely smooth creamy grain.

TRUPON OSL will help to level anionic dyeings through its dispersing and penetrating properties.

## Sulphated oil 1 (TRUPOSOL NFY)

Trumpler
simply good chemistry

# TRUPOSOL® NFY

fatliquor for automobile and upholstery leather

| | |
|---|---|
| Basis: | sulphated natural and synthetic oils |
| Appearance: | yellow brown oil |
| Charge: | anionic |
| Active matter: | approx. 65 % |
| pH value(1 : 10): | approx. 7 |
| Acid stability: | good |
| Salt stability: | good |
| Chrome stability: | medium |
| Light fastness: | excellent |
| Heat yellowing: | good |

**Properties:**

**TRUPOSOL NFY** is a semi-synthetic fatliquor which has been designed to meet the stringent demands laid down for automobile upholstery leathers.

Leathers fatliquored with **TRUPOSOL NFY** exhibit outstanding softness and fullness, coupled with a well-lubricated grain and excellent millability.

The high substantivity and low volatility that the product exhibits, allows leathers to be manufactured with outstanding fogging values whether tested by gravimetric or reflectometric methods.

These factors coupled with highly efficient exhaustion and fixation properties ensure extremely low COD levels in waste water and as a consequence an efficient and environmentally friendly fatliquoring procedure.

## Sulphated oil 2 (TRUPON KIII)

# TRUPON K III

| | |
|---|---|
| **NATURALEZA:** | Triglicéridos naturales y aditivos sintéticos sulfatados. |
| **APLICACIÓN:** | Engrasante universal |
| **APARIENCIA:** | Aceite fluido de color pardo amarillento. |
| **CARGA:** | Aniónica. |
| **SUBSTANCIA ACTIVA:** | Aprox. 75 % |
| **PH EMULSIÓN 10%:** | Aprox. 7,2 |
| **ESTABILIDAD A LOS ÁCIDOS:** | Buena |
| **ESTABILIDAD AL AGUA DURA:** | Buena |
| **ESTABILIDAD AL CROMO:** | No estable. |

El TRUPON K III se emulsiona con facilidad en 3-4 veces su peso de agua 40°/50° C obteniéndose una emulsión de color opal muy estable.

El poder emulsionante de TRUPON K III es muy elevado. Puede incorporar fácilmente hasta 100 % de su peso en aceite crudo del tipo de TRUPON CST o TRUPON PB , con lo cual puede variarse a voluntad el engrase obtenido, desde el tacto propio del TRUPON K III hasta mucho más untuoso.

El TRUPON K III es ante todo un engrasante, que al lado de un elevado poder ablandante, tiene un excelente comportamiento tanto sobre cueros al cromo, como sobre cueros al cromo recurtidos, sobre los cuales sube de manera muy regular, penetra fácilmente y se distribuye muy bien.

Gracias a este comportamiento el TRUPON K III no deja los cueros y pieles " grasientos" y las tinturas son intensas, brillantes y bien igualadas por carne y flor.

El TRUPON K III posee una excelente estabilidad en medio ácido y en presencia de aguas duras o incluso ligeramente salinas. Cuando se trabaja con condiciones desfavorables de esta naturaleza el comportamiento del TRUPON K III es muy superior al de cualquier otro aceite natural sulfatado convencional.

Cuando aprovechando la excelente estabilidad del TRUPON K III en medio ácido se requiere trabajar sobre cueros poco o nada neutralizados, téngase en cuenta que el comportamiento del engrase dependerá no solamente del pH sino de la carga del cuero más o menos catiónica. Sobre cuero al cromo puro deberá neutralizarse siempre, por lo menos moderadamente, so pena de un agotamiento demasiado rápido del engrase que impediría su buena distribución.

El TRUPON K III no provoca repousse ni tiende a amarillear por oxidación ni por acción de la luz.

## Sulphated and sulphoclhorinated oil (TRUPON DXA)

Trumpler
Creamos buena química

# TRUPON® DXA

| | |
|---|---|
| Naturaleza: | Preparado a base de aceites sintéticos sulfoclorados y sulfatados. |
| Aplicación: | Engrasante universal. |
| Apariencia: | Aceite fluido de color pardo amarillento. |
| Carga: | Aniónica. |
| Substancia activa: | Aprox. 67 %. |
| pH Emulsión 10%: | Aprox. 7.3. |
| Estabilidad a los ácidos: | Buena. |
| Estabilidad al agua dura: | Buena. |
| Estabilidad al cromo: | No compatible. |
| Solidez a la luz: | Muy buena. |
| Solidez al envejecimiento: | Muy buena. |

El **TRUPON DXA** es un engrasante aniónico preparado a partir de una mezcla cuidadosamente escogida de materias primas naturales y sintéticas.

Las emulsiones de **TRUPON DXA** se preparan muy bien con 3 a 4 partes de agua a 50/60ºC. Las emulsiones opalinas obtenidas son muy estables.

El **TRUPON DXA** puede emulsionar 20/30 % de su peso de aceites crudos.

Gracias a la parte sintética que compone el **TRUPON DXA** y a la excelente elección de materias primas naturales, las pieles engrasadas con **TRUPON DXA** están exentas de eflorescencias grasas, incluso en tiempo frío.

El **TRUPON DXA** está perfectamente adaptado para el engrase de cueros blancos y de color claro. En efecto, no favorece el amarilleamiento ni bajo la acción de la luz ni por el envejecimiento.

El **TRUPON DXA** penetra bien y se distribuye muy uniformemente dentro del cuero.

## Phosphoric ester oil 1 (TRUPON PA11)

Trumpler
simply good chemistry

# TRUPON® PA-11

| | |
|---|---|
| Basis: | Fully synthetic phosphoric esters fatliquor. |
| Uses: | Mellow handle, high gloss, softy and suede. |
| Appearance: | Yellowish brown fluid oil. |
| Charge: | Anionic. |
| Active matter: | Approx. 76 %. |
| pH Emulsion 10%: | Approx. 6,8. |
| Acid stability: | Excellent. |
| Hard water stability: | Excellent. |
| Chrome stability: | Good. Notwithstanding, TRUPON PA-11 is not prepared to be used in tanning. |
| Light fastness: | Excellent. |
| Ageing fastness: | Good. |

**TRUPON PA-11** emulsifies easily with water at 40/60ºC. However, whenever water is incorporated, the product increases its viscosity and some lumps may arise. A short stirring will then be necessary to achieve a perfect dissolution.

**TRUPON PA-11** presents opal or almost transparent emulsions, according to its preparation process. These emulsions show a high stability to acids, hard water and electrolytes.

**TRUPON PA-11** can be mixed with TRUPON or TRUPONOL in order to improve the emulsion stability.

Although **TRUPON PA-11** cannot be considered as an anti-static agent, it allows solving or decreasing problems related to static electricity.

The product hardly confers any water repellence effect, especially when used as a sole fatliquor.

Leathers and skins are soft, sheen with a fine mellow handle without showing any oiliness.

## Phosphoric ester oil 2 (TRUPON PEM)

Trumpler
simply good chemistry

# TRUPON® PEM

electrolyte-stable fatliquor

| | |
|---|---|
| Basis: | fatty acid ester products |
| Appearance: | off-white emulsion |
| Charge: | anionic |
| Active matter: | approx. 45 % |
| pH value(1 : 10): | approx. 7 |
| Acid stability: | excellent |
| Salt stability: | excellent |
| Chrome stability: | excellent |
| Light fastness: | excellent |
| Heat yellowing: | good |

**Properties:**

**TRUPON PEM** is a highly stable emulsion-type fatliquor designed for use in chrome tannage and retannage of bovine and ovine-based leathers and furskins.

**TRUPON PEM** is ideally suited for pre-fatliquoring in pickle or tannage.

**TRUPON PEM** helps disperse natural fats in the skin or hide and as a consequence lends itself to helping produce cleaner wet blues with fine grain characteristics.

**Application:**

**TRUPON PEM** can be added directly to the drum without need to pre-emulsify the product.

Quantities to be used will depend upon the type of leather to be produced, but will normally lie between 1 - 2 %, based upon pickle weight.

## Polymer and silicone oil 1 (TRUPOSIST D)

Trumpler
simply good chemistry

# TRUPOSIST® D
hydrophobing agent

| | |
|---|---|
| Basis: | polymeric, hydrophobing and fatting substances |
| Appearance: | light yellow, viscous oil |
| Charge: | anionic |
| pH value(1 : 10): | ca. 8 |
| Acid stability: | medium |
| Salt stability: | good |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOSIST D** is a polymer-based hydrophobing fatliquor designed for use in the production of high specification water resistant leather.

Leathers processed with **TRUPOSIST D** exhibit a pleasant, full and round handle with extremely high dynamic water resistance.

Leathers treated with **TRUPOSIST D** possess excellent dyeing properties without danger of greasiness, thus making it ideally suited to the production of high quality full grain and nubuck leathers.

**TRUPOSIST D** exhibits sufficient stability to salts and weakly acidic conditions to allow its use at various stages of processing, however, in order to optimise performance characteristics, it is recommended that a through neutralisation of the leather is carried out to a pH of approx. 4.8.

## Polymer and silicone oil 2 (TRUPOSIST G)

Trumpler
simply good chemistry

# TRUPOSIST® G
hydrophobing agent

| | |
|---|---|
| Basis: | polymeric, hydrophobing and fatting substances |
| Appearance: | light yellow, viscous oil |
| Charge: | anionic |
| pH value (1 : 10): | approx. 8 |
| Acid stability: | medium |
| Salt stability: | good |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOSIST G** is designed for use on leathers which require large quantities of anionic syntans, resins and vegetable-based retanning materials.

**TRUPOSIST G** is a hydrophobing agent for water resistant leathers with extremely high demands.

**TRUPOSIST G** provides excellent dyeing properties without danger of greasiness, thus making it ideally suited for the production of high quality full grain and nubuck leathers.

**TRUPOSIST G** disposes of sufficient stability to salts and weakly acidic conditions so it can be used at various stages of processing.

**TRUPOSIST G** is ideally suited for the production of washable leathers where softness and handle will be retained even after several washing cycles.

Leathers treated with **TRUPOSIST G** exhibit a pleasant, full and round handle with extremely high dynamic water resistance.

### Polymer and silicone 3 (TRUPOSIST H)

Trumpler
simply good chemistry

# TRUPOSIST® H
hydrophobing agent

| | |
|---|---|
| Basis: | polymeric, hydrophobing and fatting substances |
| Appearance: | light yellow, viscous oil |
| Charge: | anionic |
| pH value (1 : 10): | approx. 8 |
| Acid stability: | medium |
| Salt stability: | good |
| Light fastness: | excellent |
| Heat yellowing: | excellent |

**Properties:**

**TRUPOSIST H** is a hydrophobing agent designed for water resistant leathers with the highest demands.

**TRUPOSIST H** is designed for use on leathers treated with large quantities of anionic syntans, resins and vegetable-based retanning materials.

**TRUPOSIST H** provides excellent dyeing properties without danger of greasiness, thus making it ideally suited for the production of high quality full grain and nubuck leathers.

**TRUPOSIST H** exhibits sufficient stability to salts and weakly acidic conditions so it can be used at various stages of processing.

**TRUPOSIST H** is ideally suited for the production of washable leathers where softness and handle will be retained even after several washing cycles, through to the highest specification water resistant shoe upper leathers.

Leathers treated with **TRUPOSIST H** exhibit a pleasant, full and round handle with extremely high dynamic water resistance.

## Polymer and silicone 4 (TRUPOSYL ABS)

Trumpler
Creamos buena química

# TRUPOSYL® ABS

| | |
|---|---|
| Naturaleza: | Combinación especial de materias hidrofugantes con fuerte efecto ablandante. |
| Aplicación: | Cueros para empeine, nubucs, nappas donde se quieran obtener tactos blandos y "redondos" confiriendo cierta repelencia al agua. |
| Apariencia: | Pasta fluida amarillenta. |
| Carga: | Aniónica. |
| Substancia activa: | Aprox. 60%. |
| pH Disolución 10%: | Aprox. 7,0. |
| Estabilidad a los ácidos: | Excelente. |
| Estabilidad al agua dura: | Excelente. |
| Solidez a la luz: | Muy buena. |
| Solidez al envejecimiento: | Muy buena. |

**Propiedades**

El TRUPOSYL ABS además de sus propiedades de repelencia al agua, posee excelentes propiedades ablandantes. Este efecto es muy superior al de otros engrasantes de características similares. Los cueros engrasados con **TRUPOSYL ABS** poseen además una plenitud excelente y tacto muy redondo. La esmeriabilidad para artículos de nubuc es extraordinaria.

## Lecithin (TRUPON LH)

Trumpler
simply good chemistry

# TRUPON® LH

## fatliquor for all types of soft leathers

| | |
|---|---|
| Basis: | mixture of natural vegetable oils and non-ionic emulsifiers |
| Appearance: | brown, viscous oil |
| Charge: | anionic |
| Active matter: | approx. 97 % |
| pH value (1 : 10): | approx. 6,5 |
| Acid stability: | medium |
| Salt stability: | medium |
| Chrome stability: | medium |
| Light fastness: | good |
| Heat yellowing: | good |

**Properties:**

**TRUPON LH** is a highly concentrated lecithin based fatliquor.

**TRUPON LH** can be used for the fatliquoring process of chrome-tanned leathers as well as for chrome-free leathers.

Leathers fatliquored with **TRUPON LH** exhibit excellent softness together with a pleasant, round, slightly waxy handle.

## Phospholipid and synthetic oil (TRUPON PLZ)

Trumpler
Creamos buena química

# TRUPON® PLZ

| | |
|---|---|
| Naturaleza: | Combinación a base fosfolípidos naturales y engrasantes síntéticos. |
| Aplicación: | Todo tipo de artículos que requieran un buen efecto engrasante. |
| Apariencia: | Pasta viscosa de color amarillento. |
| Carga: | No iónica |
| Substancia activa: | Aprox. 50 %. |
| pH Emulsión 10%: | Aprox. 7.5. |
| Estabilidad a los ácidos: | Buena. |
| Estabilidad al agua dura: | Buena. |
| Estabilidad al cromo: | Buena. |
| Solidez a la luz: | Buena. |
| Solidez al envejecimiento: | Buena. |

**Propiedades y aplicación**

Los cueros y pieles engrasados con **TRUPON PLZ** presentan buena blandura, relleno y un tacto calido y sedoso tanto por flor como por carne.

**TRUPON PLZ** puede usarse como engrasante único cuando se requieran artículos muy blandos. Mayoritariamente se usará en combinación con otros productos de engrase. Se recomienda la combinación con TRUPON DXZ y/o TRUPON KLZ en función de los tactos y efectos deseados.

Por su excelente estabilidad al cromo, **TRUPON PLZ** puede usarse como engrase en los baños de curtición con sales de cromo o recurtición con TRUPOTAN EH. En estos casos TRUPON PLZ deberá añadirse al baño siempre previamente emulsionado con agua.

## Polymer oil (TRUPOSYL TBD)

Trumpler
simply good chemistry

# TRUPOSYL® TBD

fatliquor on polymer basis

| | |
|---|---|
| Basis: | special combination of lubricating polymers |
| Appearance: | opalescent paste |
| Charge: | anionic |
| Active matter: | approx. 60 % |
| pH value(1 : 10): | approx. 8 |
| Acid stability: | good |
| Salt stability: | good |
| Chrome stability: | good |
| Light fastness: | excellent |
| Heat yellowing: | good |

**Properties:**

Leathers prepared with **TRUPOSYL TBD** have a tight smooth grain and significantly improved fullness.

**TRUPOSYL TBD** has an excellent stability to electrolytes and can therefore be applied as a pre-fatliquor in the chrome retan float, producing a good fullness and spring in the final leather.

For waterproof leather the **TRUPOSYL TBD** is intended to be used only as a pre-fatliquor, followed by normal processing with **TRUPOSIST® D**.

Leathers treated with **TRUPOSYL TBD** demonstrate level and brilliant dyeing properties that are particularly useful for suede and nubuck leather production.

## Cationic oil (SOLVOTAN XS)

Trumpler
Creamos buena química

® XS

| | |
|---|---|
| Naturaleza: | Engrasante catiónico. |
| Aplicación: | Curtición, afelpados, tactos. |
| Apariencia: | Pasta blanca. |
| Carga: | Catiónica. |
| Substancia activa: | Aprox. 48 %. |
| pH Emulsión 10%: | Aprox. 5.5. |
| Estabilidad a los ácidos: | Buena. |
| Estabilidad al agua dura: | Buena. |
| Estabilidad al cromo: | Buena. |

El Solvotan XS proporciona unos tactos sedosos y un marcado efecto escribiente sin que se produzca un sobreengrase superficial.

Las pieles de ante engrasadas con SOLVOTAN XS se tiñen de manera uniforme y con mayor intensidad de tintura.

# ANNEX 2: Chemical Oxygen Demand

**REF 985028**

**Test 0-28 07.17**

es

## *NANOCOLOR*® DQO 15000

**Demanda química de oxígeno**

**Método:**
Determinación fotométrica de la concentración de cromo(III) tras oxidación con dicromato potásico / ácido sulfúrico / sulfato de plata

| | |
|---|---|
| Rango: | **1,0–15,0 g/L DQO (1000–15000 mg/L DQO)** |
| Longitud de onda (HW = 5–12 nm): | **605 / 620 nm** |
| Tiempo de reacción: | **2 h** |
| Temperatura de reacción: | **148 °C** |
| DQO rápida: | **30 min a 160 °C*** |

**Contenido del kit de reactivos:**
20 tubos de test de DQO 15000
1 tubo de test de solución neutra "NULL"

**Precauciones de seguridad:**
Los tubos de test contienen ácido sulfúrico 51–65 %, dicromato potásico 0,32–0,38 % y sulfato de mercurio(II) 0,37–0,74 %. La solución neutra "NULL" contiene ácido sulfúrico 51–65 %.
H314, H317, H340, H350 Provoca quemaduras graves en la piel y lesiones oculares graves. Puede provocar una reacción alérgica en la piel. Puede provocar defectos genéticos. Puede provocar cáncer.
P201, P260sh, P280sh, P303+361+353, P305+351+338, P310, P405 Pedir instrucciones especiales antes del uso. No respirar el polvo o los vapores. Llevar guantes y gafas de protección. EN CASO DE CONTACTO CON LA PIEL (o el pelo): Quitar inmediatamente toda la ropa contaminada. Enjuagar la piel con agua [o ducharse]. EN CASO DE CONTACTO CON LOS OJOS: Enjugar con agua cuidadosamente durante varios minutos. Quitar las lentes de contacto cuando estén presentes y pueda hacerse con facilidad. Proseguir con el lavado. Llamar inmediatamente a un CENTRO DE TOXICOLOGÍA / médico. Guardar bajo llave. Para más información, puede solicitar una ficha de datos de seguridad. Al agitar los tubos de DQO utilizar el recipiente de seguridad (REF 91637).

**Interferencias:**
Si el **contenido de cloruro fuera superior a 15000 mg/L** es preciso diluir la muestra. Para determinar la posible concentración de cloruro en la muestra, aconsejamos realizar un test preliminar con Tiras Reactivas QUANTOFIX® Cloruro (REF 91321).
Tras la reacción en el bloque calefactor la solución contenida en el tubo de test no debe presentar ningún enturbiamiento, ya que de lo contrario se obtendrían unos valores de DQO demasiado elevados. Debe esperarse a que se posen los enturbiamientos producidos por el sulfato de mercurio precipitado. Al interpretar los resultados del análisis debe tenerse en cuenta la fuerte dilución.

El método no es aplicable al análisis de agua de mar.

**Procedimiento:**
Accesorios requeridos: *NANOCOLOR*® bloque calefactor, pipeta de émbolo con puntas

***Advertencia:*** *En las muestras con alto contenido de cloruro es importante agitar el tubo de test* ***antes*** *de añadir la muestra, para poner en suspensión el sedimento.*

**según DIN ISO 15705 a 148 °C**

Abrir el tubo de test, **mantenerlo inclinado**, cubrir **lentamente** el contenido con **0,2 mL (= 200 µL)** de solución de muestra.
Enroscar fuertemente el tapón del tubo de test, sujetar el tubo por el tapón de rosca, colocarlo en el recipiente de seguridad, agitarlo y colocarlo en el calefactor. Poner éste en funcionamiento.
Al cabo de 2 h sacar el tubo de test del bloque calefactor, agitarlo otra vez transcurridos unos 10 min *(todavía caliente)* y dejarlo enfriar a temperatura ambiente.
Limpiar el tubo de test por el exterior y medir.

**DQO rápida a 160 °C**

Abrir el tubo de test, **mantenerlo inclinado**, cubrir **lentamente** el contenido con **0,2 mL (= 200 µL)** de solución de muestra.
Enroscar fuertemente el tapón del tubo de test, sujetar el tubo por el tapón de rosca, colocarlo en el recipiente de seguridad, agitarlo y colocarlo en el calefactor. Poner éste en funcionamiento.
Al cabo de 30 min sacar el tubo de test del bloque calefactor, agitarlo otra vez transcurridos unos 10 min *(todavía caliente)* y dejarlo enfriar a temperatura ambiente.
Limpiar el tubo de test por el exterior y medir.

** A diferencia de las condiciones descritas en la norma ISO 15705, la DQO rápida se caracteriza por una mayor temperatura de digestión y un tiempo de reacción reducido. Por tanto, se recomienda comparar los resultados de la DQO rápida de vez un cuando con medidas hechas bajo las condiciones de la norma DIN ISO 15705 (150 ± 5 °C / 2 h ± 10 min).*

**Medición:**
Para fotómetros MACHEREY-NAGEL ver el manual, test 0-28.

**Fotómetros de otros fabricantes:**
Con otros fotómetros comprobar si es posible la medición de tubos de test. Comprobar el factor para cada tipo de aparato mediante medición de los estándares.

**Control de calidad:**
*NANOCONTROL* DQO 15000 (REF 92528) o Multitest Agua de infiltración (REF 925013)

**Almacenaje:**
Conservar en lugar fresco y seco. Proteger el ensayo contra los rayos del sol.

**Literatura:**
Métodos normalizados alemanes para el examen de aguas, aguas residuales y lodos (DIN 38 409 - H41-1)

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